THE CRYSTAL STRUCTURES OF SOME ORGANIC MOLECULES

THESIS
PRESENTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE
UNIVERSITY OF GLASGOW
BY

ROBERT F. BRYAN B.Sc.

AUGUST 1957.

ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

Preface.

This work was undertaken at Glasgow University in the Department of Chemistry. It is a pleasure to acknowledge the profit derived from the supervision of Dr. J.C. Speakman at all stages of the work described here.

Thanks are due to Professor J.M. Robertson for his interest in this study ; and to various other members of the Department, in particular Dr. H.M.M. Shearer, I am indebted for stimulating discussion and valuable advice.

To the Department of Scientific and Industrial Research I am indebted for a maintenance allowance over the period this work has been in progress.

Mr. J. Findlay has been of considerable assistance in the production of diagrams in the text.

Pure samples of the para-alkoxybenzoic acids used were kindly supplied by Professor Brynmor Jones and Dr. D. Gray of the University College of Hull.

INDEX

I N D E X

SECTION THREE (cont'd)

PART TWO

SECTION ONE

SECTION TWO

SECTION TWO (CONT'D)

SECTION THREE

List of Figures present in the text.

SUMMARY

Summary.

This thesis describes crystallographic and other work carried out during the past three years, in the laboratories of Professor J. M. Robertson, under the supervision of Dr. J.C. Speakman.

It is divided into two parts. Part One describes work on the structure of two acid salts of cinnamic acid, and is sub-divided into three sections.

Section One contains some remarks on the nature of the hydrogen bonding found in acid salts of the type MHA_2, with especial reference to the infra-red spectra of the acid cinnamates, an interpretation of which is attempted.

Sections Two and Three, deal with work on the structures of potassium and ammonium hydrogen dicinnamates. Use was made of the Isomorphous Replacement method of phase determination, and the structure of the ammonium salt has been elucidated by two dimensional Fourier methods and refined by ($F_o - F_c$) syntheses. Bond lengths and angles etc. are given and discussed.

Part Two contains the results of an investigation of some members of the homologous series of para-alkoxybenzoic acids.

Section One gives a list of the cell constants for the acids between para-methoxybenzoic acid, and para-nonyloxy-benzoic acid, which have been determined by X-ray methods.

Section Two describes an analysis by two dimensional Fourier methods of para-methoxybenzoic acid. This analysis though terminated prematurely, has reached a fair degree of

precision, and bond lengths and angles etc. are given and discussed.

Section Three gives details of a preliminary analysis, by the Fourier transform method, of the structure of para-ethoxybenzoic acid, which has been elucidated in (h0l) projection.

PART ONE

The Structure of the Ammonium and Potassium Acid Salts of Cinnamic Acid

SECTION ONE

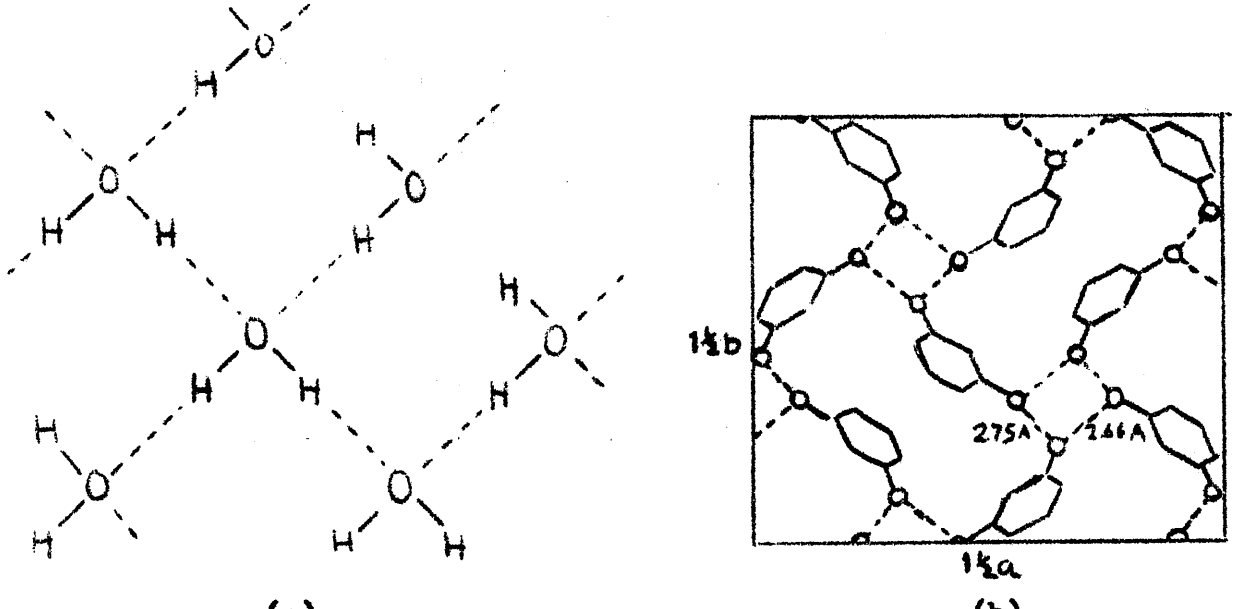
Introductory Remarks on Hydrogen Bonding in the Acid Salts

Hydrogen Bonding and the Acid Salts.

Introductory.

The 'hydrogen bond' is the name given to a type of liaison in which a hydrogen atom, or a proton, forms a link between two electronegative atoms or ions. The linkage has some of the characteristics of a normal chemical bond though in all instances its energy is much less than that of a covalent bond, whilst being at the same time greater than that of the very weak van der Waal's attractive force.

That it is a directed linkage, and that in a lattice a system of hydrogen bonds may, co-operatively, exert a considerable influence on the structure of a compound is shown by the examples of ice and of α- resorcinol.



(a) (b)

Fig.I.Structures of (a) ice, and (b) α-resorcinol, showing the directional nature of the hydrogen bond systems.

Both are very open structures of correspondingly low density, which at higher temperatures give way to more closely packed arrangements, in which significantly, hydrogen bonding still plays a large part.

Such linkages may be formed with oxygen, nitrogen, fluorine or chlorine, acting as the electronegative unit, but only hydrogen appears to be capable of acting as the binding unit; this presumably because of its small size and the absence of any electron higher than the Is orbital.

It will be sufficient to consider only the hydrogen bonds between oxygen atoms to illustrate the nature of the phenomenon. The bonds may be inter-molecular, as in the instances given above, or they may be intra-molecular, as in the case of salicylic acid.

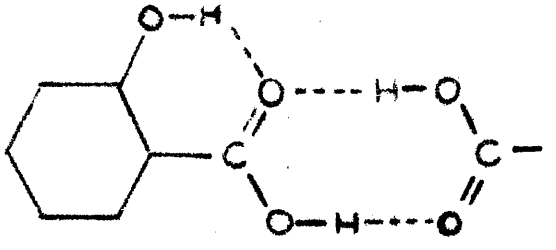


Fig. 2. Structure of salicylic acid showing intra, and inter-molecular hydrogen bonding.

Where such inter-molecular or intra-molecular association occurs deviations from the expected physical properties of the compound concerned are often observed. Thus in colligative phenomena, abnormal results are often obtained in the opposite sense to those found where dissociation takes place. The chemical properties of such compounds are frequently

affected also, and the observation of effects of this general nature is diagnostic of the presence of hydrogen bonding.

Other methods of establishing the presence of hydrogen bonding are of two main types. Firstly by direct structure determination, and secondly by the observation of certain vibrational phenomena connected with the nature of the linkage.

Since there is normally but a limited amount of electron density around the hydrogen atom, X-ray diffraction is not a useful means of revealing the presence of a hydrogen atom in a hydrogen bond ; and since its nuclear charge is also small electron diffraction methods are also difficult to use for the purpose. Consequently, what is commonly revealed by both these methods is a close approach between two heavier atoms which can be satisfactorily explained only by the assumption of a hydrogen bond between them. Various accurate measurements of the O ... O distance in a great many hydrogen bonded systems have now been obtained by both these means. (i)

More exact information as to the actual site of the hydrogen atom in the linkage can be got by application of neutron diffraction techniques, and several structures involving hydrogen bonds have been studied by this means.

Most important of these from a theoretical point of view, is probably the recent work of Peterson and Levy on the structure of heavy ice (ii), where the model suggested by Pauling (iii) is upheld. Also relevant in the present connection is the as yet unpublished work

of Bacon on the structure of potassium hydrogen bis-phenylacetate, (iv) which is discussed below.

Vibrational methods are chiefly those of infra-red absorption spectroscopy.

Several effects are noteworthy. Thus the characteristic vibrational frequency of the O-H bond is commonly different in the same molecule in states where hydrogen bonding does or does not occur. In monomeric formic acid for instance, the O-H vibrational frequency has a value of 3680 cm^{-I}, whereas in the dimer this value is reduced to some 3080 cm^{-I}. This characteristic reduction may extend to give frequencies as low as I900 cm^{-I}, and in the case of the acid salts to give still lower values. (v)

Various relations have been proposed between this drop in frequency and both the strength and the length of the linkage (vi), and these are discussed below in relation to the acid salts. The diagram below, after Nakamoto, Margoshes, and Rundle, illustrates one such relation.

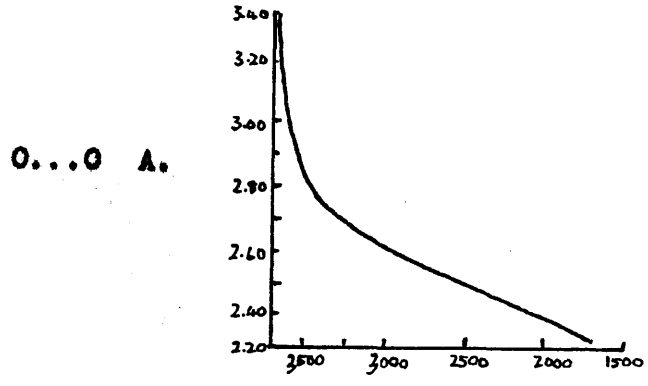


Fig.3. Variation of O-H frequency with O...O separation in O-H..O bonds.

Vibrational transitions in the infra-red may have an increased intensity in bonded molecules, and the bands are frequently broadened (vii).

Compression also has an effect in altering the vibrational frequency, and this may become more important as the bond becomes more nearly symmetrical . (viii)

The results of these various measurements give a range of values for the O ... O separation in different compounds of some 3.3 to 2.4 A. In all but a few limited cases which will be discussed later the bond is asymmetrical in that the hydrogen atom is to be found nearer to one oxygen atom than to the other, leading to a formulation O - H ... O .

Thus for ice each oxygen atom is found to have two nearest neighbours at a distance corresponding to a normal O - H covalent bond length, and two somewhat further removed, and only on this basis can such facts as its high dielectric constant, and residual entropy at 0° K. be explained.

Many attempts have been made to account for the energy of the hydrogen bond, but none has been entirely satisfactory both because of the severe approximations which it is necessary to make in wave-mechanical calculations,and the low total energy of the bond which in the case of an O - H ... O bond is of the order of six k.cal.

There are three factors presently held to exercise an important influence on the energy of the bond. (ix) These are :

1. Electrostatic energy
2. Delocalisation energy
3. Repulsive energy .

Early theoretical treatments of hydrogen bonding tended to assume that electrostatic effects could account for the total energy of the bond (x). Later wave - mechanical calculations by , inter alia, Coulson and Danielson (xi), Pauling (xii) , and Ellison and Shull(xiii), have shown that while electrostatic energy accounts for a considerable proportion of the total energy , it cannot represent the complete situation. An ideally electrostatic arrangement would involve the three atoms in a co-linear system if the maximum energy was to be achieved, and several instances are known where the hydrogen atom is removed from the line of the two oxygen atoms, e.g. as in salicylic acid and α - resorcinol.

Further, the increase in intensity of the infra-red absorbtion around 3μ due to the O-H vibration, beyond the thirty per cent or so, increase attributable to electrostatic effects, demands that as the hydrogen vibrates in the bond considerable fluctuations of charge take place between the outer atoms, or, which is to say the same thing, there is much delocalisation of electrons in the bond.(xiv).

If only four electrons are assumed to be involved in the system O_I ... H ... O_2 ; two in the bond O_I - H , and two as a lone pair, then Coulson writes (ix) five different valence bond structures can be considered :

$- O_I - H \ldots O_2 <$ (I)

$- \bar{O}_I - \dot{H} \ldots O_2 <$ (II)

$- \dot{O}_I \quad \bar{H} \ldots O_2 <$ (III)

$- \bar{O}_I \quad H - \dot{O}_2 <$ (IV)

$- O_I \quad \bar{H} \quad \dot{O}_2 <$ (V)

where (4) and (5) represent contributions in excess of the purely electrostatic contributions from (I), (2), and (3), and involve charge transfer.

As a result it can be shown that in a bond of length 2.8 A. the contribution from structures (4) and (5) represent only some 2 % of the total energy, whereas in a bond of 2.5 A. their contribution may be as much as IO % .

The diagram, after Coulson and Danielson , shows how in a bond of length 2.5 A. the contribution of the covalent forces to the total bond energy increases as the hydrogen moves away from O_I towards the centre of the bond.

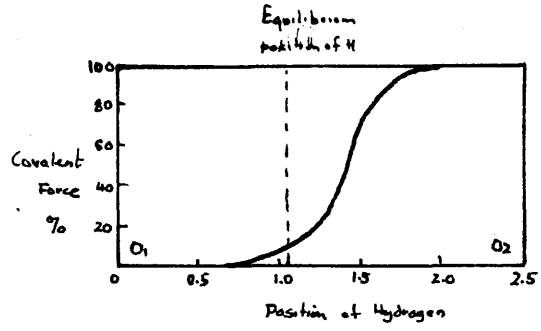


Fig. 4.

Similar results have been obtained by Tsubomura using rather less approximations and a more elegant method of calculation (xv₂).

The third of the forces involved is the repulsive force between the atoms taking part in the bond. It acts in the opposite sense to that of the first two forces considered and is probably the most important factor in determining the length and hence the nature of the bond. It is not easy to obtain a reliable estimate of the magnitude of the force since the concept of conventional van der Waal's radii is not applicable. In the normal long bond such as in ice, the repulsive forces will be between the charge cloud on the hydrogen atom and those on each of the two oxygen atoms. The charge cloud of the hydrogen atom then keeps the two oxygen atoms at a distance from one another where no covalent forces of any significance can be brought into play between their electron clouds.

In the case of all the symmetrical hydrogen bonds so far reported however, the central unit is not a hydrogen atom but a proton, whose charge radius is effectively zero which presumably allows the two oxygen atoms to come sufficiently close together for covalent interactions of some importance to occur . It is seen both theoretically and practically that the point at which these forces become sufficiently strong to induce the proton to take up a central position is around 2.45 A. Nakamoto, Margoshes, and Rundle give the diagram overleaf which illustrates the variation of the distance O - H, with decrasing O ... O separation. The value derived for a symmetrical linkage from this is about 2.4 A. (vi)

Practical evidence is afforded by a consideration of the structures of maleic acid, and the maleate anion. (xvi)

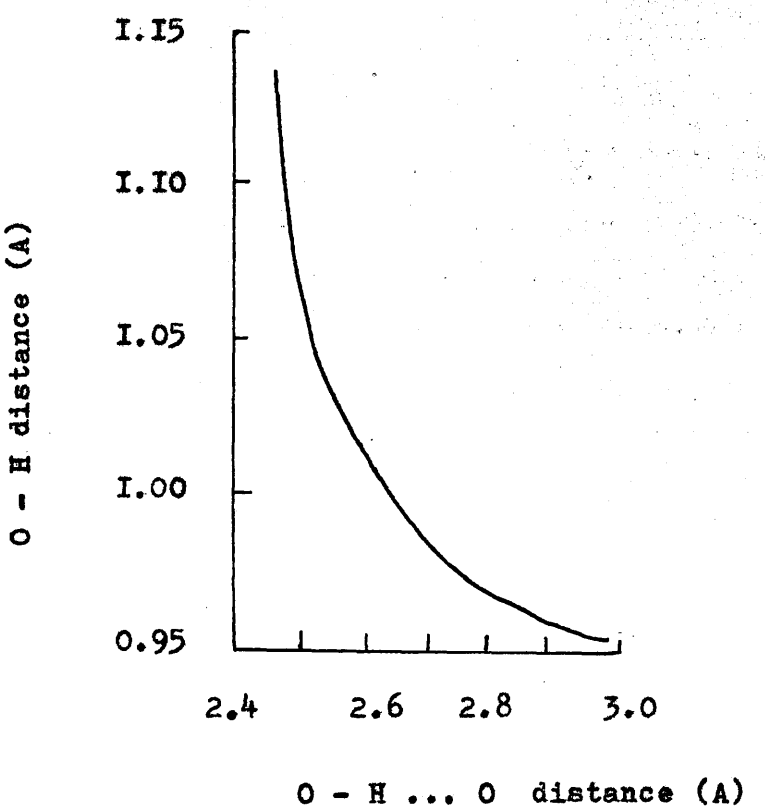


Fig. 3a.

Diagram, after Nakamoto, Margoshes, and Rundle, showing the variation in the distance O - H as a function of the distance O - H ... O , in this type of hydrogen bond.

In the first of these the measured O ... O separation is 2.46 A. and the hydrogen atom is nearer to one oxygen than to the other. In the anion where the distance O ... O is 2,44 A. the proton is established as being in a central position in the bond.

A similar state of affairs exists in the structure of nickel dimethylglyoxime, where the separation is again 2.44 A. Here the exact position of the proton is not known, but it must be very likely to be at the centre of the bond.

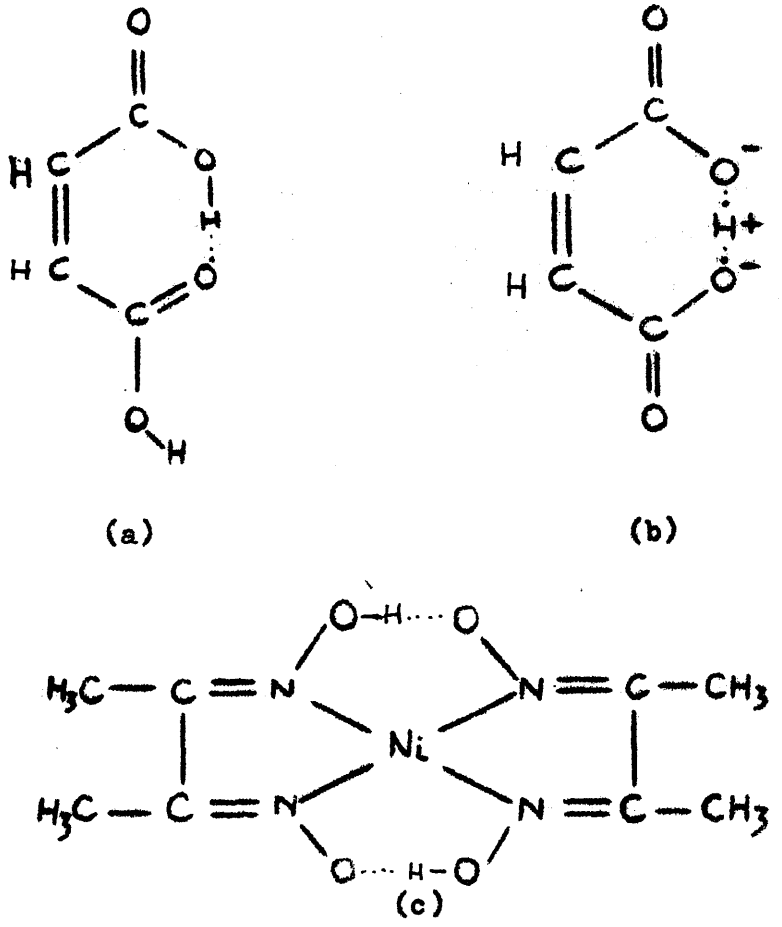


Fig. 5. Structural formulae of (a) maleic acid, (b) acid maleate anion, and (c) nickel dimethylglyoxime.

Table summarising the results of X-ray analyses of various acid salts.

A C I D S A L T S

MHA_2 type

Acid (HA)	M	Space-group	Evidence for $\bar{1}$	Z	Hydrogen Bond: Sym. by,	Hydrogen Bond: O...O (Å)
Phenylacetic	K	I2/a (Ia)	+	4	$\bar{1}$	2.55
p-OH-benzoic*	K	P?/c (Pc)		2	$\bar{1}$	2.61 ±.05
Benzoic	K, NH_4	C?/c (Cc)	++	4	$\bar{1}$	2.51
Cinnamic	NH_4, K	C2/c (Cc)	++	4	$\bar{1}$	2.46
Anisic	Rb, K	Pbcn	(+)	4	$\bar{1}$ (2)	?
o-NO_2-benzoic	Rb	$P\bar{1}$ (P1)	?+	1	$\bar{1}$(?)	<3.4
p-NO_2-benzoic	K	C2/c (Cc)		4	$\bar{1}$(?)	?
Carbonic (Trona)*	Na	C2/c (Cc)	+?	4	$\bar{1}$	2.53±.03 2.50±.02
Salicylic*	NH_4, K	$P2_1/c$	(+)	4	-	
Acetic	Na	Ia3	(+)	24	2	?
Maleic	K				m	2.45(?)

(*Acid salt hydrated.)

The hydrogen bond in the acid salts.

The type of hydrogen bond found in many of the acid salts of monocarboxylic aromatic acids is possessed of three notable features. (xvii).

Firstly, the bond involves charged oxygen atoms and presumably also a proton. Connected with this is the shortness of the O... O separation, where the distance varies with some considerable uncertainty between 2.6 and 2,4 A. These are longer than the critical limit laid down of 2.44A. for a symmetrical bond, except in the case of the acid cinnamates discussed in the present work, which stucture is the only one in which the refinement has been carried out by the use of (F_o - F_c) syntheses ; but all are shorter than the type of bond found say in carboxylic acid dimers.

The third peculiarity is that by crystallographic requirement each bond must have a centre of symmetry, or in one case must be disposed about a two-fold axis.

All these facts are relevant in suggesting that the bonds in these salts may be symmetrical, but before concluding that this is so it is first necessary to dispose of several objections which have been raised against such an assumption.

The first objection concerns the choice of space group. In all the structure determinations on these salts so far published the space group was not uniquely defined by the absences in the X-ray spectra, and a choice was possible between a centred and a non-centred space group. The choice of the centred space group was supported by statistical tests which are more fully described in the section describing the structural work on the acid cinnamates; and appeared to

be justified by the outcome of the analyses. Let it be sufficient to remark here that a salt of this general type, potassium hydrogen di-anisate has been since found to belong to the space group Pbcn which is uniquely determined (xviii).

Although the space group itself may be centred, it has been argued that the proton need not occupy the centre of symmetry. If for instance it was permanently oscillating between two potential minima disposed about the centre, a 'time average' symmetry could be achieved.

For a single hydrogen bond Coulson has deduced that the shape of the potential energy curve will be as shown in the diagram overleaf, and he considers it unlikely that a double minimum such as that suggested is to be found. Indeed as the O ... O separation decreases the shape of the potential energy curve becomes more nearly symmetrical.(xv) The amplitude of vibration of the proton may nevertheless be considerable ca 0.5 A.

The 'time average' symmetry is therefore unlikely.

The proton might also be supposed to be more closely attached to one oxygen atom than to the other, with, throughout the lattice a statistical distibution in space leading to an apparent symmetry. This would approximate to a random distribution of acid and anion throughout the lattice, and Davies and Thomas suggested that this was probably the case from a consideration of the infra-red absorbtion spectrum of phenylacetic acid , that of potassium phenylacetate, and that of potassium hydrogen bis-phenyl-acetate. (xix). This last they considered could be interpreted as a superposition of the spectra of the first two compounds.

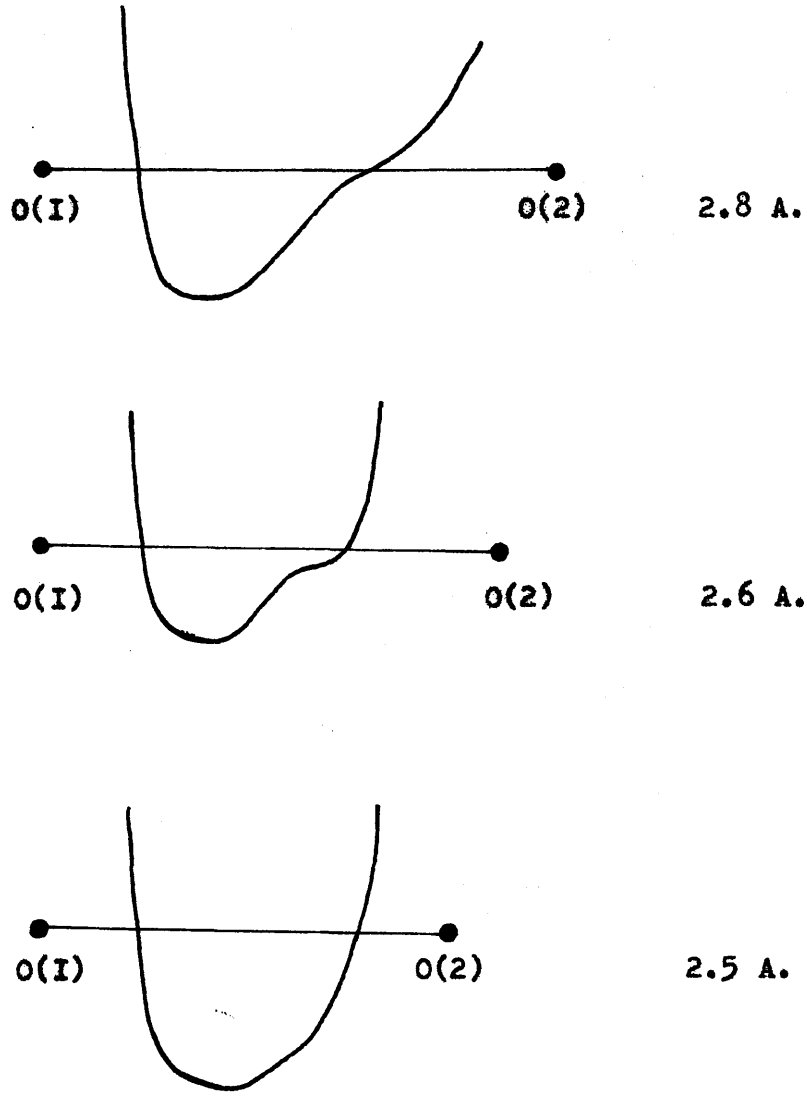


Fig 4a.

Graph giving possible potential energy curves for the motion of a proton along the O(I)....O(2) axis in hydrogen bonds of various lengths, (after Coulson).

Davies and Thomas however in preparing their sample of the acid salt appear to have first melted the crystals and then allowed them to cool. It has since been shown that the structure of the acid salt breaks down on such treatment and their results are not therefore significant.

Hadzi (xx) and ourselves have shown that the spectra of these acid salts is in no way such a straightforward superposition, as is borne out generally by the illustrations of some of these spectra given overleaf. The spectra of the derivatives of phenylacetic acid are by Hadzi, those of the derivatives of cinnamic acid are by ourselves.

It is worthwhile digressing to consider some aspects of these spectra.

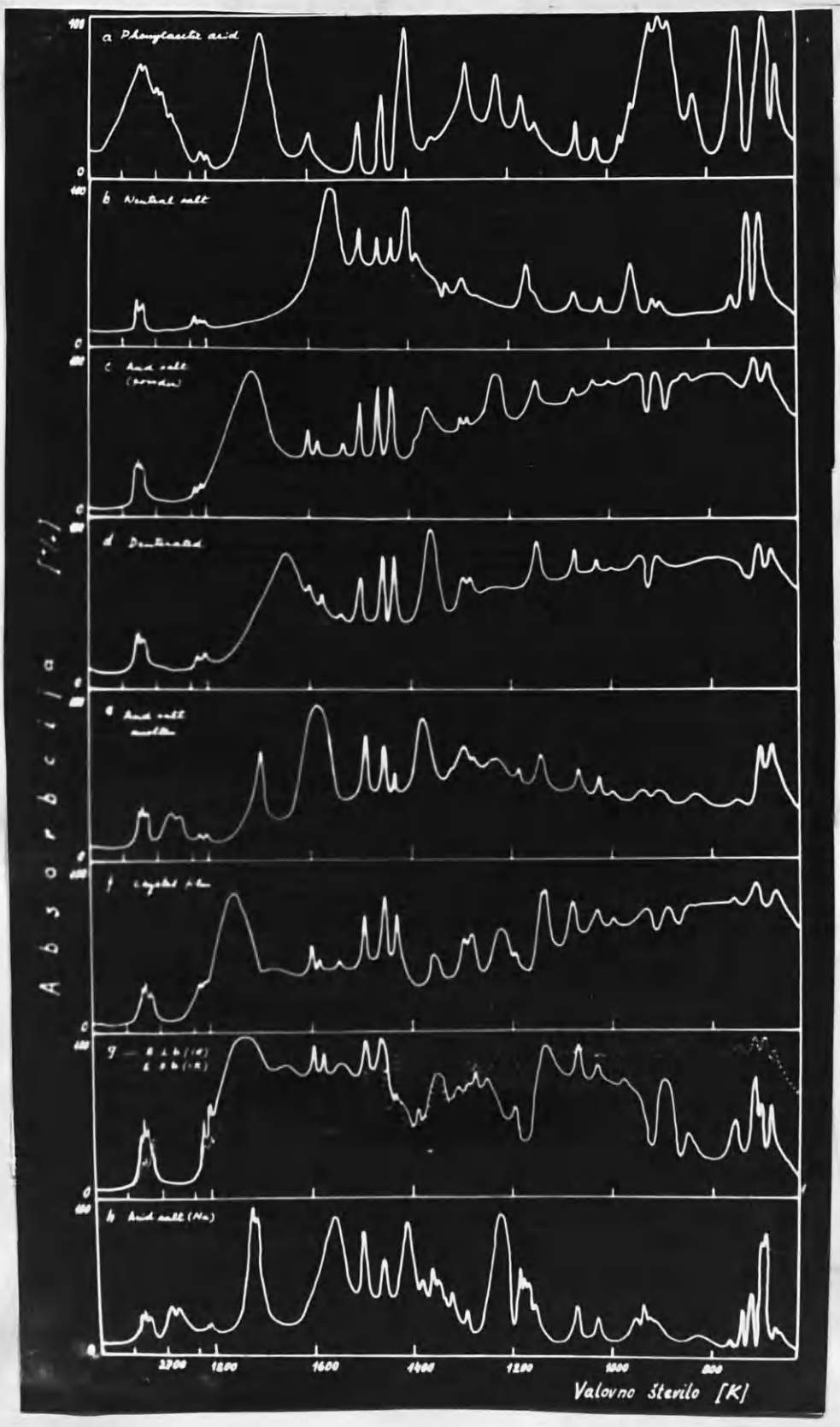
Dealing with the spectra of phenylacetic acid etc. Hadzi makes the following points.

1. The O-H frequency at 950 cm^{-1} which is found in the spectra of dimerised carboxylic acids is present in the spectrum of phenylacetic acid, but not in that of the acid salt.

   (Its absence from the spectrum of the acid salt is however open to doubt, particularly since the resolutien of the region around 950 cm^{-1} is very poor)

2. There is in the acid a very strong band at ca 1700cm^{-1} which is absent from the neutral salt, but is present slightly displaced in the acid salt. In the acid this band is attributed to a C=O frequency, but in the acid salt is of less certain attribution, being discussed in more detail below.

Fig. 6. Infra-red absorbtion spectra of phenylacetic acid and its derivatives(after Hadzi) .



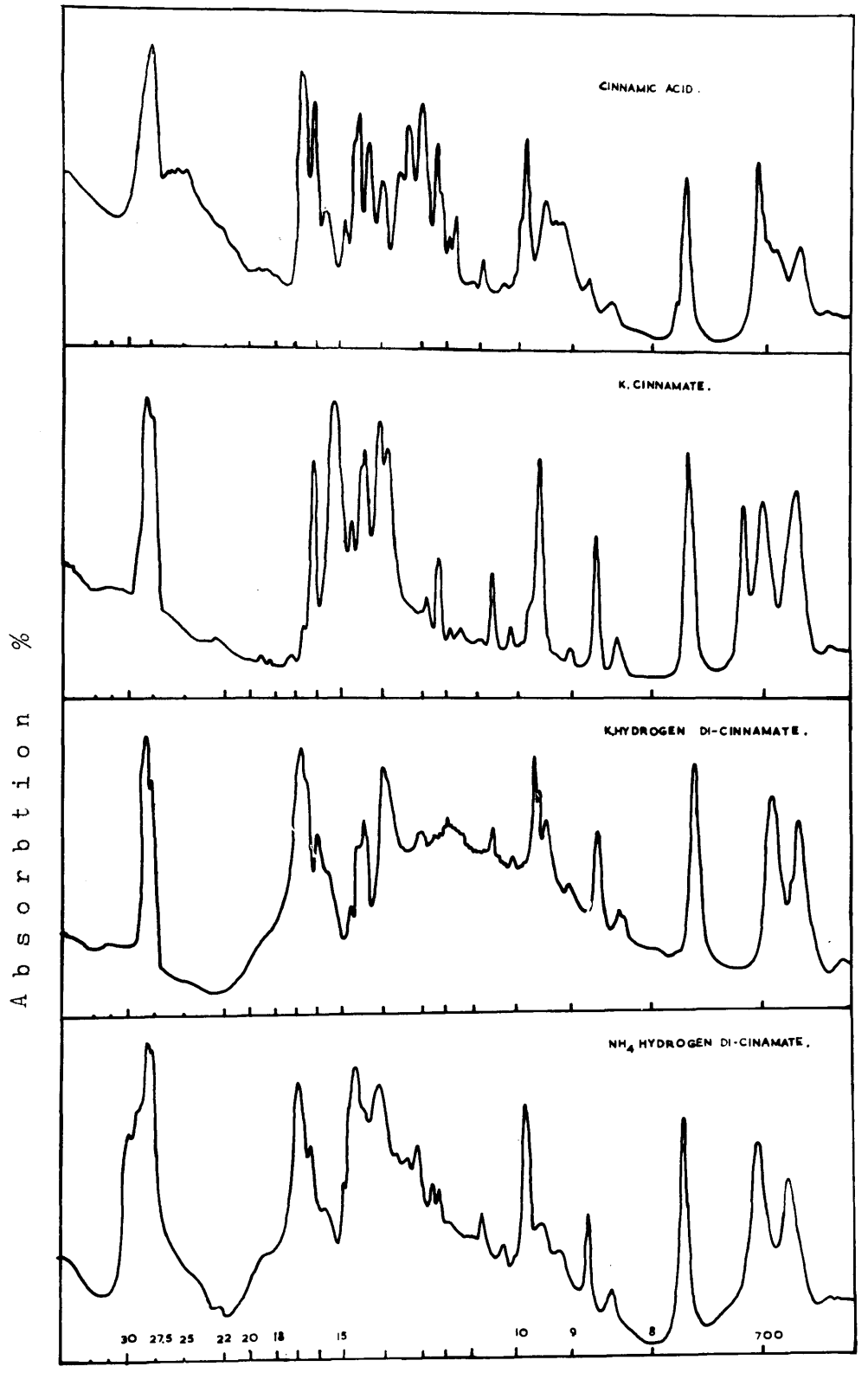


Fig. 7. Infra-red absorbtion spectra of cinnamic acid and various salts.

3. There is in the spectra of the neutral salt a band ca 1560 cm^{-1} which is attributed to the ionised carboxyl group. This band is absent from the spectra of both acid and acid salt.

4. A group of bands occurring between 1560 and 1600cm^{-1} in the spectrum of the acid salt might possibly be thought to be associated with the anti-symmetrical vibration of the COO^- group, but these bands are not present in the spectrum of the deuterated acid salt, and in consequence are held to be in some way connected with an O-H-O frequency of some kind.

   There are apparently no bands in the spectrum of the acid salt corresponding to the symmetrical and anti-symmetrical vibrations of the COO^- group.

5. There are no peaks between 3000 and 1800 cm^{-1} in the spectrum of the acid salt directly attributable to any O-H stretching frequency.

These facts are sufficient to prove that the contentions of Davies and Thomas are erroneous. The spectrum of the molten acid salt shown by Hadzi is sufficient to show how the error arose.

The assignment of the large peak in the region of 1700 cm^{-1} mentioned in point2 as being of interest can now be discussed with reference to the spectra of the acid cinnamates. On deuteration of the bis-phenylacetate the peak retained its shape but shifted to a frequency lower by some 50 cm^{-1} which suggests that it is not a pure O-H stretching frequency, since a much larger shift would then be expected on deuteration. That a shift is observed

however argues that the peak is more likely to be due to an interaction between a weakened O-H stretching frequency and a predominant C=O frequency, and this conclusion is further strengthened by a consideration of the large peak at I700 cm^{-I} in the spectrum of cinnamic acid, and that at I680cm^{-I} in the spectra of both potassium and ammonium hydrogen di-cinnamate. This latter is seen to have a definite shoulder associated with it in the region of I900 cm^{-I} which is very probably connected with the O-H stretching vibration.

What this implies in terms of the O ... O separation can be seen by considering the graph of $\Delta\nu_{OH}$ against d(O ... O) due to Magat in this instance (xxi). This assumes a fundamental O-H frequency of 3750 cm^{-I} for a free OH group. The value of I900 cm^{-I} leads to an O ... O separation of ca 2.46 close to the upper limit of length for a symmetrical bond, whereas that of I560 cm^{-I} tentatively suggested by Hadzi, leads to a separation of ca 2.42 - 2.43 A., both of which values confirm the unusually short O ... O distance observed of 2.39 A.

Speculatively , if the separation were about 2.40 A. such a treatment would lead to a value for the O-H stretching frequency of ca I050 cm^{-I} , and if the amplitude of vibration of the oxygen atoms was at all significant, ca 0.I - 0.2 A., the congested nature of the spectrum over the region I400 - 950 cm^{-I} might be explicable on these terms. Hadzi suggests that this congestion is perhaps due to some overtone of the fundamental lattice vibrations, but while the phenomenon is certainly characteristic of these acid salts it remains unexplained. It will be noted

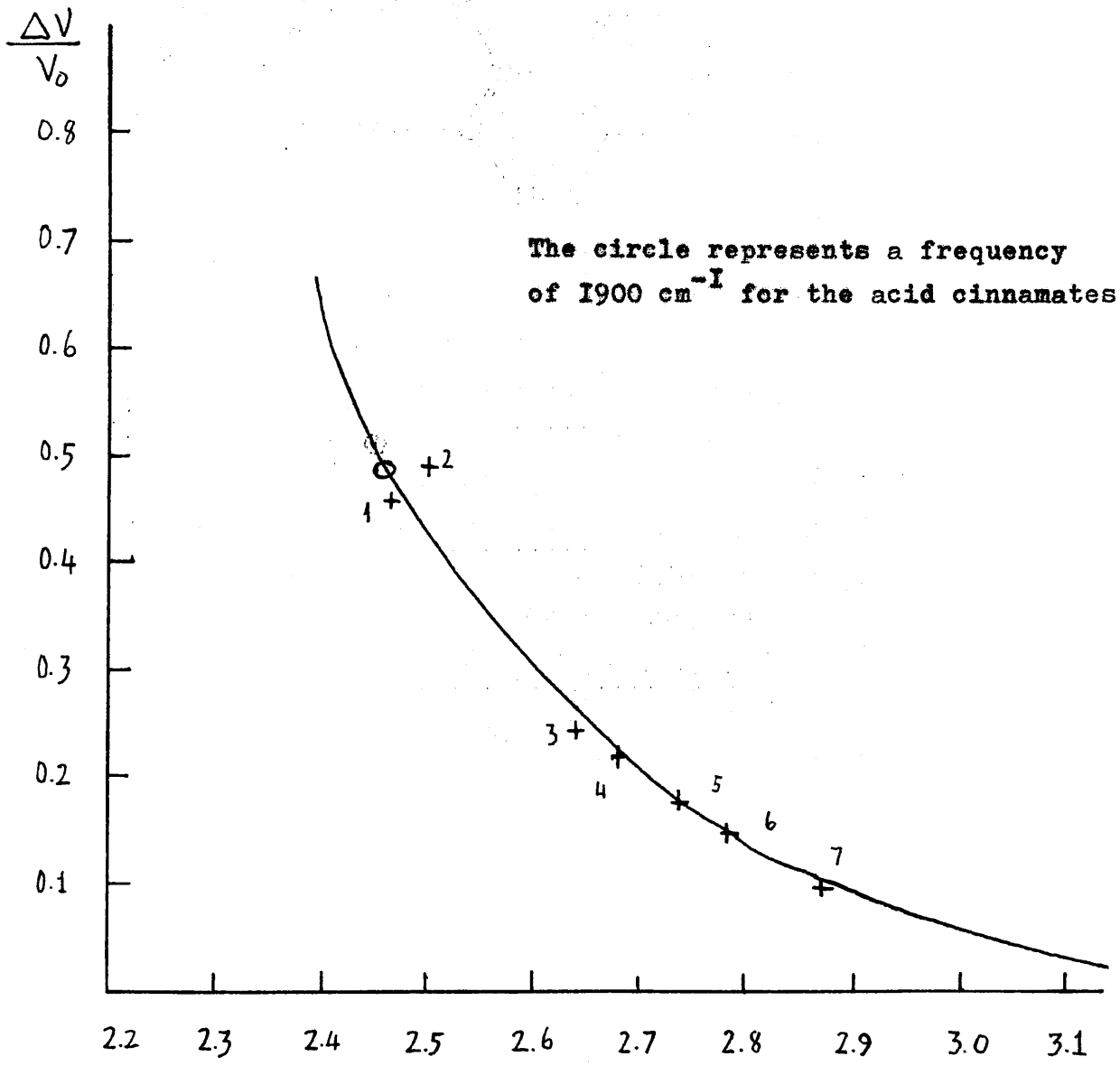


Fig. 8.

Graph (after Magat) illustrating the relation between $\Delta\nu/\nu_0$ and the separation O...O A. assuming $\nu^0_{OH} = 3750$ cm^{-I}.

Legend : I. Maleic acid
2. Oxalic acid dihydrate.
3. Succinic acid
4. Adipic acid
5. Formic acid
6. Acetic acid
7. Oxalic acid dihydrate

that the congestion is not so acute in the spectra of the acid cinnamates, and this clarifies the position around 950 cm^{-1} where it will be recalled Hadzi claimed a difference in the spectra of parent acid and acid salt. This region in the acid cinnamates is sufficiently close in appearance to that of the parent acid for some doubt to be present as to the correctness of Hadzi's assertion.

There is now available an important piece of positive information regarding the structure of ~~deuterated~~ potassium hydrogen bis-phenylacetate. The work of Bacon already referred to (iv) reveals that the hydrogen ion is situated at the centre of symmetry, and hence at the centre of the bond, and that its amplitude of vibration, although considerable, is entirely isotropic. By analogy therefore it is likely that the hydrogen bond in the other acid salts of this general structural type is also genuinely symmetrical.

References : Part One , Section One.

I. J.M. Robertson : 'Organic Crystals and Molecules' New York, I953.

2. S.W. Peterson, H.A. Levy : Acta Cryst.,(I957), I0 , 70.

3. L. Pauling : J. Amer. Chem. Soc.,(I935), 57 , 2680

4. G.A. Bacon : personal communication to Dr. J.C. Speakman.

5. R.C. Lord, R.E. Merrifield : J. chem. Phys.,(I953),2I, I66.

6. K. Nakamoto, M. Margoshes, R.E. Rundle : J. Amer. Chem. Soc., (I955), 77, 6480.
R.E. Rundle, M. Parasol; J. chem. Phys.,(I952),20, I487.

7. S.A. Francis : ibid,(I95I), I9, 505.
H.L. Frisch, G.L. Vidale; ibid, (I956), 25, 982.

8. A.R. Ubbelohde : J. Chim. phys., (I949), 46, 429.

9. C.A. Coulson : Research, (I957), I0, I49. (To which the plan of this introductory section owes much.)

I0. E.J.W. Vervey : Rec. Trav. chim. Pays-Bas, (I942), 62, I27.
M. Magat : Ann.Phys.,Paris, (I936), 6, I08.

II. C.A. Coulson, U. Danielson : Ark. Fys., (I954), 8, 239 & 245.

I2. L. Pauling : J. Chim. phys.,(I949), 46, 435.

I3. F.O. Ellison, H. Shull : J. chem.Phys.,(I955), 23, 2348.

I4. N.D. Coggeshall : ibid, (I950), I8, 978.

I5. H. Tsubomura : Bull. chem. Soc. Japan, (I954), 27, 445.

I6. E.J.W. Vervey : Rec. Trav. chim. Pays-Bas,(I94I), 60, 587.
H.M.E. Cardwell, J.D. Dunitz, L.E. Orgel : J.,(I953), 3740.
L.E. Godycki, M.E. Rundle : Acta Cryst.,(I953), 6, 487.
S.F. Darlow : paper to Conference on Hydrogen Bonding Llubljana, I957.

I7. J.C. Speakman : J. , (I949), 3357.
J.C. Speakman, J.M. Skinner, ibid (I95I), I85.

I7. Skinner J.M., G.M.D. Stewart, J.C. Speakman, ibid,(I954), I80.
J.C. Speakman, work in progress.

I8. J.M. Skinner, personal communication.

I9. M. Davies, W.J.O. Thomas, J.,(I95I), 2858.

20. D. Hadzi, A. Novak; Nuovo Cimento, N.3 del Supplemento al Vol.2. Serie X., 7I5.

2I. M. Magat : paper to Paris Conference I.U.C. I954.

PART ONE

SECTION TWO

Potassium Hydrogen Di-cinnamate

Potassium hydrogen di-cinnamate.

Summary of previous work.

A fair amount of work had been done on the structure of this compound before a decision was made to attempt the isomorphous replacement method of phase determination as a solution to the problem (i).

In this summary of the state of affairs existing before I took up the work, reference may be made to several techniques etc., which may be more fully, and more appropriately described later.

The salt had been prepared by mixing alcoholic solutions one mole of potassium hydroxide and two moles of cinnamic acid. Crystals suitable for X-ray work had been got by recrystallising the original product from alcohol. These were in the form of thin plates with the (OOI) face developed.

The unit cell dimensions had been calculated from single crystal rotation photographs about the three principle axes, and the space group symmetry had been determined from oscillation photographs, and from moving films of the Weissenberg type. The crystal data, and other relevant information are summarised in the table below.

Intensities had been measured for both (hOl) and (hkO) using the Robertson multiple film technique (ii), and making visual estimates of the integrated intensity . These reflexions were re-estimated by myself at the beginning of my work, and the data used in structure determination, were an average of the various separate estimations.

Table of Crystal Data for potassium hydrogen di-cinnamate.

$KH(C_9H_7O_2)_2$. M = 336.5 F(000) = 696

Monoclinic prismatic.

a = 37.7
c = 7.65
b = 5.74 A.
β = 93.5°

ρ observed , I.342 ; calculated on the basis of four formula units per unit cell , ρ = I.340

Systematic absences : (hkl) ; h + k = 2n + I
(h0l) ; l = 2n + I (h = 2n + I)
(0k0) ; k = 2n + I .

Space group ; Cc (C_s^4), or C2/c (C_{2h}^6) .
The latter was chosen.

Structural work.

In determining the structures of other acid salts of this type considerable information had been gained from a study of the two dimensional Patterson projections, and accordingly Patterson syntheses had been carried out using the (h0l) and (hk0) data for the acid cinnamate.

In the c axis projection, the vector distribution had been complicated by the overlap of two molecules, but a reasonable interpretation had been achieved, and a trial structure derived by Speakman had been refined by Fourier methods to give a value of R = 35 % .

No reasonable interpretation of the b axis Patterson projection had been achieved.

The plan decided on at this stage, when I took up the work, was to ascertain whether the corresponding ammonium salt was isomorphous with the potassium compound, and if so, to make use of the isomorphous replacement method to solve the phase problem. The more detailed refinement of the structure would then be carried out on the ammonium salt in order to avoid the diffraction effects associated with the presence of the "heavy" potassium ion.

Whilst this was being decided an attempt would be made to find a suitable trial structure to satisfy the (h0l) data for the potassium salt.

The b axis projection.

The intensity data for this zone are dominated by a very strong low order reflexion, associated with the plane of indices $(\bar{4},0,2)$, for which $|F_o| = 243$. If the potassium ion be taken as the origin of co-ordinates, then the contribution of this ion to the structure factor $(\bar{4},0,2)$ is +58, which gives two possible values, +185, or -301, for the contribution from the anion. The former value was assumed to be the more likely, both from the appearance of the Patterson projection, and because it requires a lower value for the unitary structure factor of the plane.

Several trial structures based on this assumption, that of a molecule appearing in side perspective with its main axis lying close to the $(\bar{4},0,2)$ plane, were tried in an effort to produce an acceptable measure of agreement between the observed and calculated data, but none of these proved very satisfactory, although electron density projections bearing a certain resemblance to such a model could be got

by means of Fourier syntheses of the observed structure amplitudes together with the calculated phases.

It became evident after a few such trials that this model was fundamentally wrong, and this was confirmedwhen the isomorphism of the two salts having been established, an estimate of the magnitude of $|F_o|$ $(\bar{4},0,2)$ for the ammonium salt showed it to be greater than for the potassium salt, implying that the contributions of anion and cation are opposite in phase. In fact the contribution of the anion is 7I % of the total possible value, a figure sufficiently high to be remarkable.

No further work was done on the potassium compound after this point, attention being confined to the ammonium salt, the structural analysis of which is described in the following section.

References

(i). J. Skinner, G.M.D. Stewart, and D. Storer ; B.Sc theses presented to the University of Glasgow

(ii).J.M. Robertson, J. Sci. Instr. I953, 20 , I75.

PART ONE

SECTION THREE

Ammonium Hydrogen Di-cinnamate

Ammonium hydrogen di-cinnamate.

Introductory and preparation.

This compound was first reported by Carrick (i), and is easily prepared by mixing stoichiometric quantities of ammonium hydroxide, and of cinnamic acid dissolved in an excess of alcohol ; when crystals of the acid salt at once separate out. This appears to be the only product of the reaction.

The salt is stable at room temperature, though some superficial loss of ammonia seems to take place over prolonged periods of time. At higher temperatures it decomposes with loss of ammonia.

Crystals suitable for X-ray work were got by recrystalisation of the original batch from 95 % alcohol. These crystals formed as thin plates with the face (I00) developed, and showed pronounced cleavage in a direction parallel to this. Under the polarising microscope the crystals showed straight extinction.

Cell dimensions etc.

Single crystal rotation photographs, taken with copper K (λ = I.54A), and cobalt K (λ = I.79A) radiation were used to determine the unit cell dimensions. Oscillation and Weissenberg photographs about the principle axes were used to find the symmetry elements present, and to determine the angle β. The results of these measurements and other relevant information are contained in the table of crystal data given below.

Table of Crystal Data for ammonium hydrogen di-cinnamate.

$NH_4(C_8H_7COO)_2.H$. M = 313 F(000) = 664

Monoclinic prismatic.

a = 37.87 (± 0.12)
b = 5.84 (± 0.02)
c = 7.62 (± 0.03) A. $\beta = 95.5° (\pm 1°)$

The salt is isomorphous with its potassium analogue.
Volume of unit cell = 1674 A^3.
ρ observed 1.05 ; calculated on the basis of four formula units per unit cell, ρ = 1.045.

Systematic absences : (hkl) ; h + k = 2n + 1 .
(h0l) ; l = 2n + 1, (h = 2n + 1)
(0k0) ; k = 2n + 1.

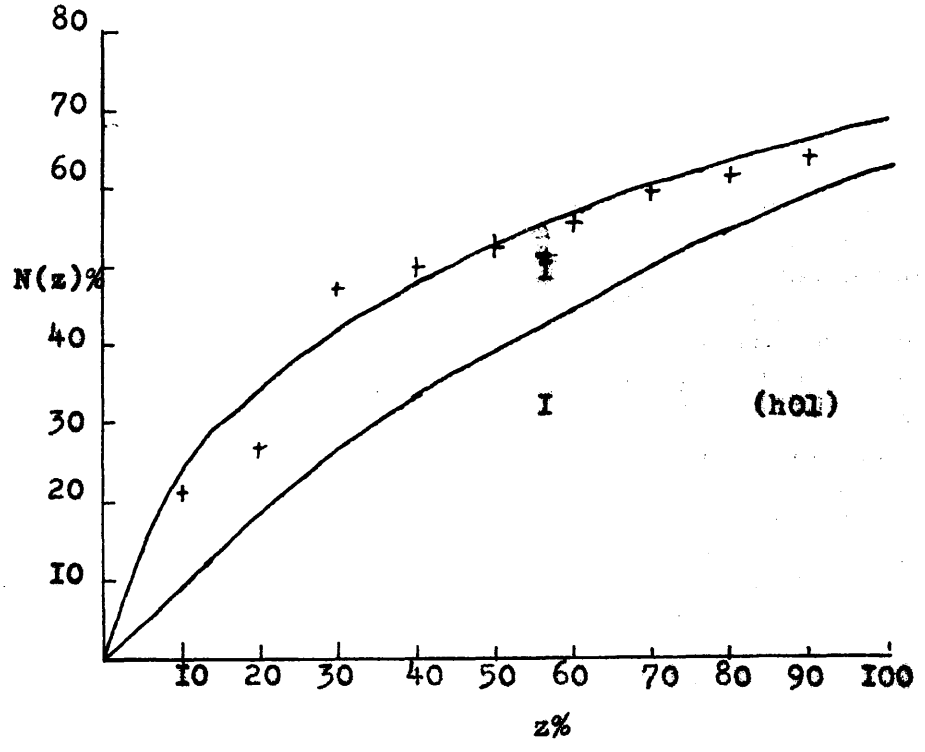
Space group : Cc (C_s^4) , or C2/c (C_{2h}^6) .

Absorption coefficient for X-rays, (λ = 1.54 A.), 8.55 per cm.

Choice of Space Group.

On the basis of the systematic absences of reflections, alternative space groups are ; Cc or C2/c. The space group C2/c was chosen. Since this choice in fact determines the necessity for a centro-symmetrical hydrogen bond, as discussed in the introductory section, it is as well to give the reasons for this selection, and the evidence in support of it.

The use of a centred space group in similar circumstances in the case of the other acid salts studied had been originally



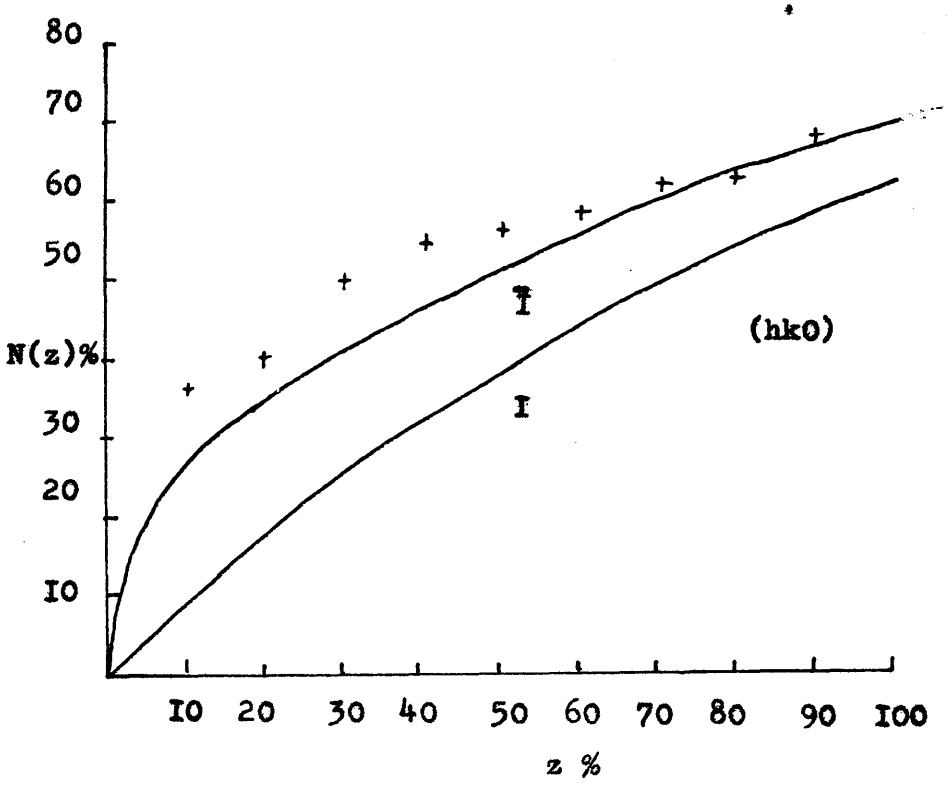


Fig. 9. Diagram illustrating the Howells, Phillips, and Rogers's test for centro-symmetry as applied to the data for (h0l) and (hk0) for ammonium hydrogen dicinnamate.

justified by the successful outcome of these analyses, and there seemed little reason why this should not also be the case here. In addition the use of a centred space group greatly reduces the amount,of computation required. These however, are merely reasons of precedent and of expediency, and further evidence would normally be needed.

There have been proposed various tests to establish the presence of a centre of symmetry in a crystal based on the differing distributions of intensities occurring in centred and non-centred cases.

Wilson (ii) has observed that for a non-centro-symmetrical crystal the mean value of the structure amplitudes is greater than that for a centro-symmetrical crystal. He has calculated that the ratio of the square of the mean structure amplitude to the mean intensity should have the values $\pi/4$, (0.785), and $2/\pi$ (0.637), for the two types of crystal respectively.

Howells, Phillips, and Rogers (iii), show that the fractions N(z) of reflexions whose intensities are equal to or less than a fraction z of the local average, are given by the function :

$$N(z) = I - \exp(-z),$$

for a non-centro-symmetrical crystal, and by the function :

$$N(z) = \operatorname{erf}(\tfrac{1}{2}z)^{\frac{1}{2}}$$

Both these tests were applied to the (h0l) and (hk0) intensities. The Wilson ratio for (h0l) was 0.595, and for (hk0) was 0.489. The N(z) curve for each zone is shown in the diagram overleaf. Both clearly indicate a centro-symmetrical distibution.

It is perhaps worth mentioning at this stage that the salt potassium hydrogen di-anisate, which is of the same structural type has the space group Pbcn , which is uniquely determined by the X-ray spectra.

Collection and measurement of intensity data.

Intensity data for (h0l) and for (hk0) were collected photographically using the Robertson multiple film technique. In each case a pack of five films was used, the reduction factor for the passage of copper radiation through one film and two sheets of Black paper being 3.25.

In this way 105 reflexions were recorded in (hk0) out of a total of 156 theoretically accessible to copper radiation. In (h0l) 148 out of a possible 183 reflexions were recorded. This gives a ratio of reflexions to positional parameters of ca 7:1 in (h0l) , and ca 5:1 in (hk0) , excluding hydrogen atoms.

The reflexions were indexed by means of two dimensional reciprocal lattices.

The estimation of the integrated intensity of each reflexion was done visually, and the results of three separate estimations for each zone were averaged. As a further check the reflexions were also arranged in order of increasing intensity and by this means a few minor errors were corrected. The range of intensity measured was of the order of 1,000 to 1 in each instance.

Structure amplitudes on a relative scale were obtained by applying the usual corrections for mosaic crystals, and these were placed on an absolute scale by a method due to Wilson (iv).

At a later stage in the refinement of the c axis projection absorbtion corrections were applied to the (hkO) intensities , based on a consideration of the path of an X-ray beam reflected from the centre of the crystal. (v). This was to correct for the somewhat anomalous shape of the crystal used , some 0.3 x 0.03 mm in cross-section. No thicker crystal than this could be obtained owing to the ready cleavage of all specimens when any attempt at cutting was made. No errors obviously due to extinction were found as the analysis proceeded.

The Isomorphous Replacement Method of phase determination applied to the acid cinnamates.

The structure factor expression for the (OIO) projection of the space group C2/c is given by :

$$F = 4f_i \sum \cos 2\pi (hx_i + lz_i) + 8f_j \sum \cos 2\pi (hx_j + lz_j)$$

where x_i, z_i, are the fractional coordinates appropriate to atoms occupying four-fold special positions in the unit cell, and x_j, z_j, are the fractional coordinates of atoms in general positions. f_i and f_j are the appropriate scattering functions and the summation is made over all the atoms in the unit cell.

If it be taken as characteristic of isomorphous substances that corresponding atoms occupy identical positions in the unit cell, then the only difference in the structure factor expressions for the potassium and the

ammonium salt will be that f_i will be in the one case the scattering function for potassium, and in the other the scattering function for the ammonium ion. Since in this projection these ions are situated at centres of symmetry which may be taken as the origin of coordinates the numerical value of the expression

$$4f_i \sum \cos 2\pi (hx_i + lz_i)$$

is known, and is equal to 4fi.

There are then two values of the function ,

$$8f_j\, 8f_j \sum \cos 2\pi (hx_j + lz_j)$$

which will give the same value of $|F_o|$ in the case of each of the two salts, and one of these two values will be common to both. It is this value, taken in conjunction with the value of $4f_i$, which enables the sign of $|F_o|$ to be determined.

In the (OOI) projection the situation is not quite so straightforward, since there is a possible ambiguity in the position of the cations. From the projected distance of the O - H ... O separation , 2.35 A., derived from the b axis projection it seemed that the two oxygen atoms in question were more likely to be related by a centre of symmetry than by a two fold-axis, which means that the cations must be assumed to lie on the two-fold axis,and also be free to take up any position along it. However previous calculation of structure factors for the (OOI) projection with the potassium ion at various positions had indicated that the position y = ½ was the most probable . In addition the actual mode of application of the method

compensates for any slight shift from this position, since it is the agreement between two sets of values for the contribution of the anion to the structure factor which is in fact the phase determinant. It was therefore thought justifiable to use the method in this zone.

The b axis projection.

Using the method described above phase constants could be unambiguously assigned to 79 of the I48 observed structure amplitudes. These terms were used as co-efficients in a double Fourier series which was computed using the Robertson stencil method, at intervals of 3° (0.3I5 A.) along the a axis, and at intervals of 6° (0.I28 A.) along the c axis, giving the electron density at 900 points in the asymmetric unit.

The electron density function for (hOl) is given by the expression :

$$\rho(h0l) = \frac{1}{A}\left[F(000) + 2\sum_{2}^{\Delta_h} F(h00)\cos 2\pi h x + 2\sum_{2}^{\Delta_l} F(00l)\cos 2\pi l z + 2\sum_{2}^{\Delta_h}\sum_{2}^{\Delta_l}\left\{ F(h0l)\cos 2\pi(hx+lz) + F(\bar{h}0l)\cos 2\pi(-hx+lz)\right\}\right].$$

The electron density contour map plotted from these data gave a recognisable representation of the molecule but no resolution of individual atoms, save two, was achieved owing to the steep angle of inclination of the molecule in projection.

Atomic centres were chosen from the projected density distribution using as a model a planar unit with conventional bond lengths and all interatomic angles taken as I20°.

The structure factor expression for (OIO) is given by :

$$F = 4f_i \Sigma \cos 2\pi (hx_i + lz_i) + 8f_j \Sigma \cos 2\pi (hx_j + lz_j) .$$

in the terms already defined. The scattering function used for the carbon and oxygen atoms at this point was the compounded McWeeny function (vi), with an isotropic factor $B = (8\pi\bar{u}^2) = 5.I$ derived by Wilson's method (iv). This value of B is to be compared with that of 3.5 derived by similar means for the potassium salt.
The ammonium ion was treated as a simple nitrogen atom and the correspondingly modified McWeeny function was used here.

This led to a value for $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$, of some 62 %, a value which is somewhat high. The reasons for this did not appear until a later stage in the refinement, but it was held to be encouraging that there were present none of the glaring anomalies between observed and calculated values which had so disfigured earlier attempts on this zone in the potassium compound.

As a result of this calculation of structure factors I03 terms were now held to be phase determined and a second Fourier synthesis was carried out, followed by structure factor calculation which improved the agreement somewhat giving R = 47 % .

It was now evident that little progress could be made by continuing to use the planar model initially postulated, since several alternative trial structures based on it failed to improve the agreement notideably.

Assuming the side chain atoms to lie on a plane making an angle of some 15° with the plane containing the benzene ring, produced an immediate and marked improvement in the situation, the value of R being reduced to the more acceptable level of 25 % .

Refinement by successive Fourier syntheses followed by structure factor calculation was continued till no further sign changes of any significance took place in the terms. The electron density resulting from the sixth and final such synthesis is shown in the projection overleaf. The value of the residual at this stage was 20 % .

The refinement was continued by means of (F_o - F_c) syntheses. Hydrogen atoms were postulated at distances equivalent to I.I A. from the appropriate carbon atoms and the structure factors were recalculated before proceeding with these.

The first such synthesis revealed shifts required in the coordinates of nearly all atoms none of them however very substantial. The temperature factor B for the carbon atoms appeared to require increasing to 5.5, and that for the oxygen atoms to a value around 6.0, although the situation around the carboxyl group was very obscure owing to the considerable overlap of atoms in the group. Six such syntheses were carried through and a final value of R = 14.7 % resulted. In the final calculation of structure factors the scattering function for the oxygen atoms was multiplied by 8.5/8.0 to allow for the presence of an extra half electron on these atoms. This process had been used in the case of previous structure determinations

Fig. IO.

Projection of electron density on (hOl) for ammonium hydrogen di-cinnamate. Contour levels represent one electron increments. The one electron level is dotted.

Fig. IO.

Projection of electron density on (hOl) for ammonium hydrogen di-cinnamate. Contour levels represent one electron increments. The one electron level is dotted.


a/4
c/2
0
0
1
2
3
Å

in the series (vii) , but it is doubtful whether this is a valid means of correcting for this. The situation is dealt with more fully in Appendix I.

The following atomic coordinates resulted .

Atom	x/a	z/c
NH_4	0.0000	0.2500
O(I)	.0289	.0943
O(2)	.047I	.034I
C(I)	.0525	.0730
C(2)	.0903	.I396
C(3)	.I053	.I945
C(4)	.I397	.2580
C(5)	.I474	.3509
C(6)	.I829	.4226
C(7)	.2I00	.4068
C(8)	.2030	.3092
C(9)	.I686	.24I7

****

The c axis projection.

The application of the Isomorphous Replacement Method as described above yielded the signs of 55 out of the 105 observed structure amplitudes. This number would have been larger but for the smaller number of observed reflections in the case of the potassium salt.

The 55 terms were used as co-efficients in a double Fourier series, evaluated using the Robertson stencils, at intervals of 3° (0.312 A.) along a.sinβ and at intervals of 6o (0.098A.) along b.

The electron density in (hkO) is given by the expression

$$\rho(hk0) = \frac{1}{A}\left[F(000) + 2\left\{ \sum_{2}^{\infty}{}^{h} F(h00)\cos 2\pi hx + \sum_{2}^{\infty}{}^{k} F(0k0)\cos 2\pi ky \right\} + 4\sum_{1}^{\infty}{}^{h}\sum_{1}^{\infty}{}^{k} F(hk0)\cos 2\pi hx \cdot \cos 2\pi ky \right].$$

The electron density contour map plotted from the data obtained in this way gave a fair indication of the atomic positions of the atoms in the benzene ring, but there was again considerable overlap of atoms in the regions around the double bond and carboxyl group. The position of the ammonium ion was confirmed as being x = 0, y = ½ .

Structure factor calculation using the expression :

$$F = 8 f_j \sum_{j=1}^{N} \cos 2\pi hx_j \cdot \cos 2\pi ky_j$$

gave a good measure of agreement between the observed and calculated values, when the scattering functions derived from the b axis projection were used. Successive Fourier refinement of the zone was carried through till all signs

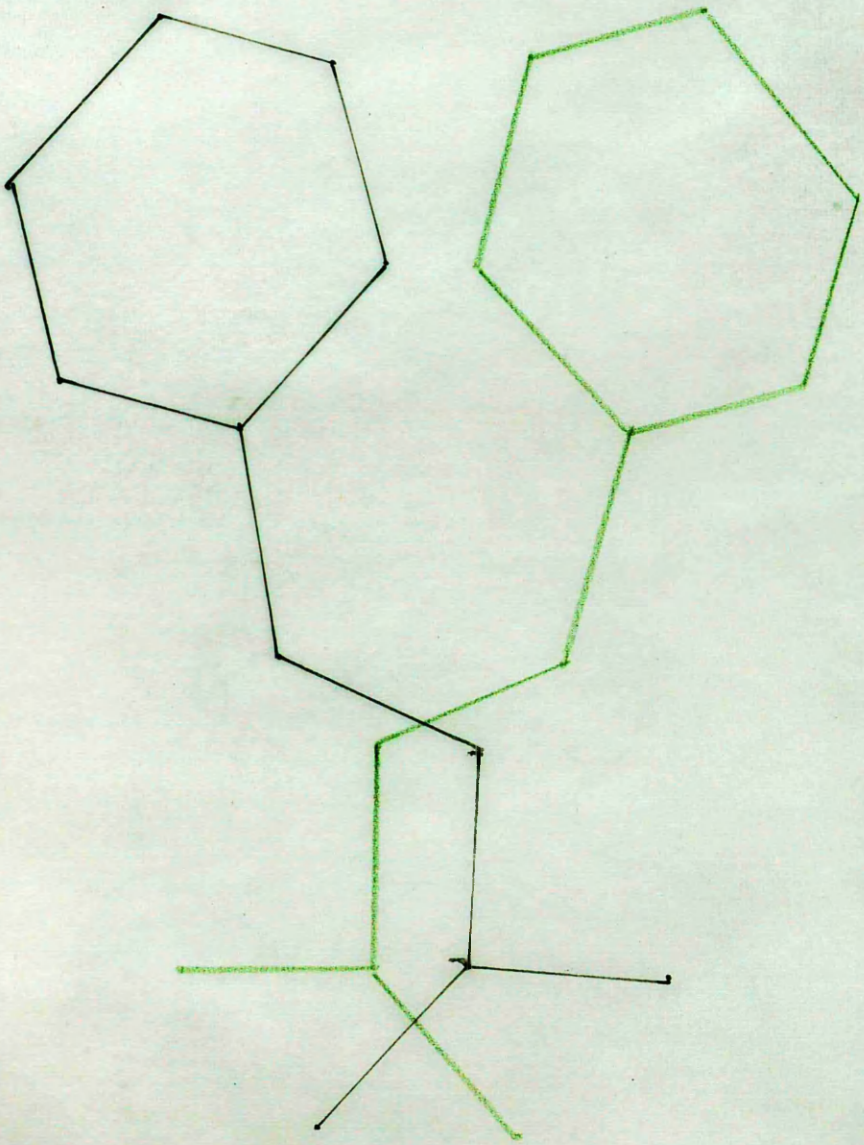
remained constant. The projection of the electron density re resulting from the fifth synthesis is shown overleaf.

As for the b axis projection the refinement was furthered by the use of difference syntheses, allowance being made for the presence of hydrogen atoms in the same manner.

Again as in the b axis projection the interpretation of these syntheses was complicated by overlap in the region of the carboxyl group in particular. The refinement in consequence was very slow and proceeded somewhat from expedient to expedient. Absorbtion corrections were applied to the intensity data but without any great improvement resulting. The scattering function for the ammonium ion was altered to allow for a greater and more concentrated electron density, the method of achieving this is described in Appendix I ; but still the rate of refinement was very slow. In seven cycles of refinement by this means the value of R fell from 22% initially to I8% .
This is not excessive but somewhat disappointing since comparable accuracy had been achieved in other members of the series (vi), with the use of straightforward Fourier refinement.

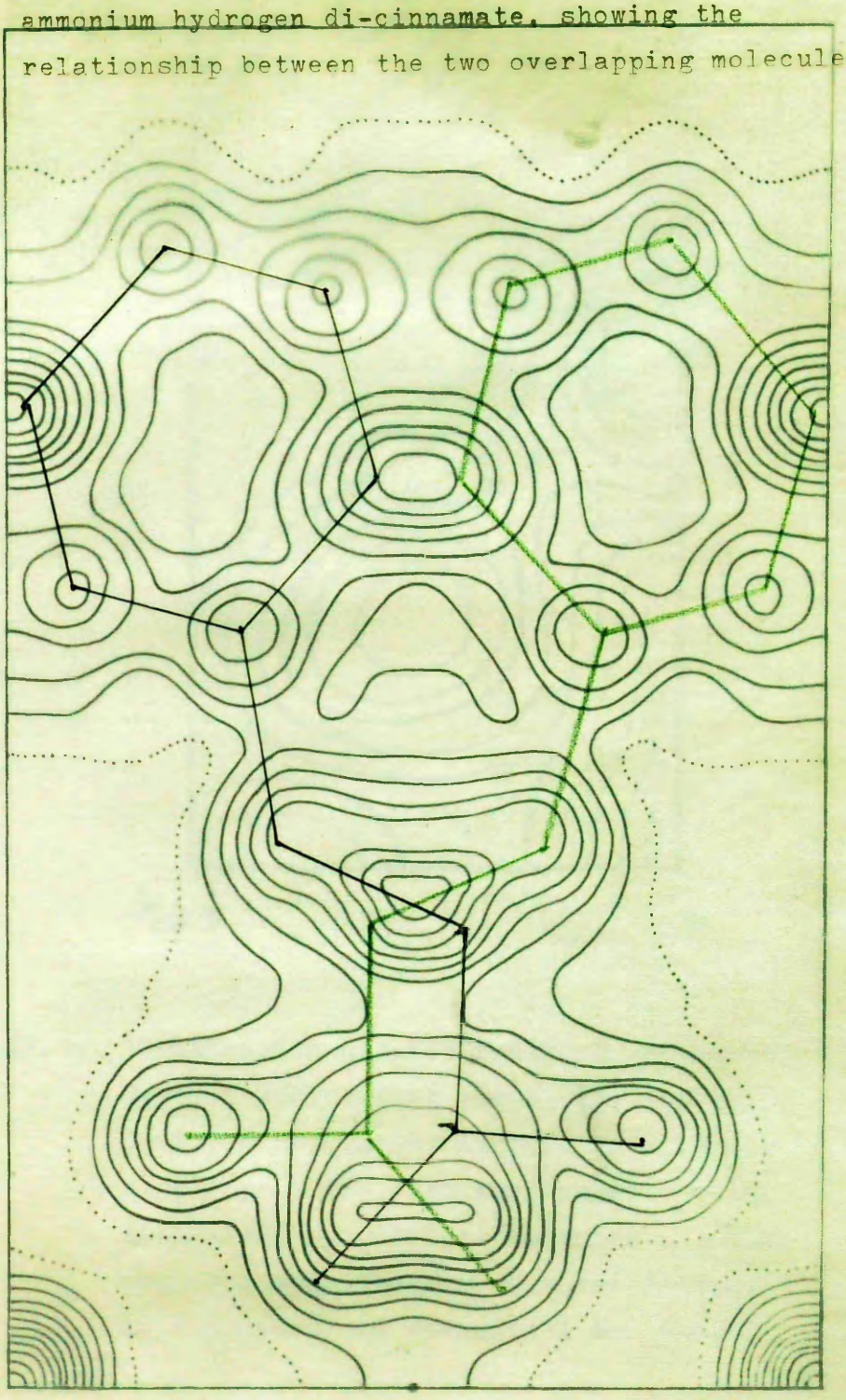
Since the main features in the residual density maps were a peculiar distribution around the carbon atom of the carboxyl group and around the oxygen atom involved in the hydrogen bond, which feature is illustrated overleaf, various combinations of different positions of these atoms were included in structure factor calcu lations, but no great improvement resulted. It is possible that the thermal motion of either the oxygen atom or of the carboxyl carbon atom is not wholly isotropic but it was felt that any

Fig. II. Projection of electron density for (hk0) for ammonium hydrogen di-cinnamate, showing the relationship between the two overlapping molecules.



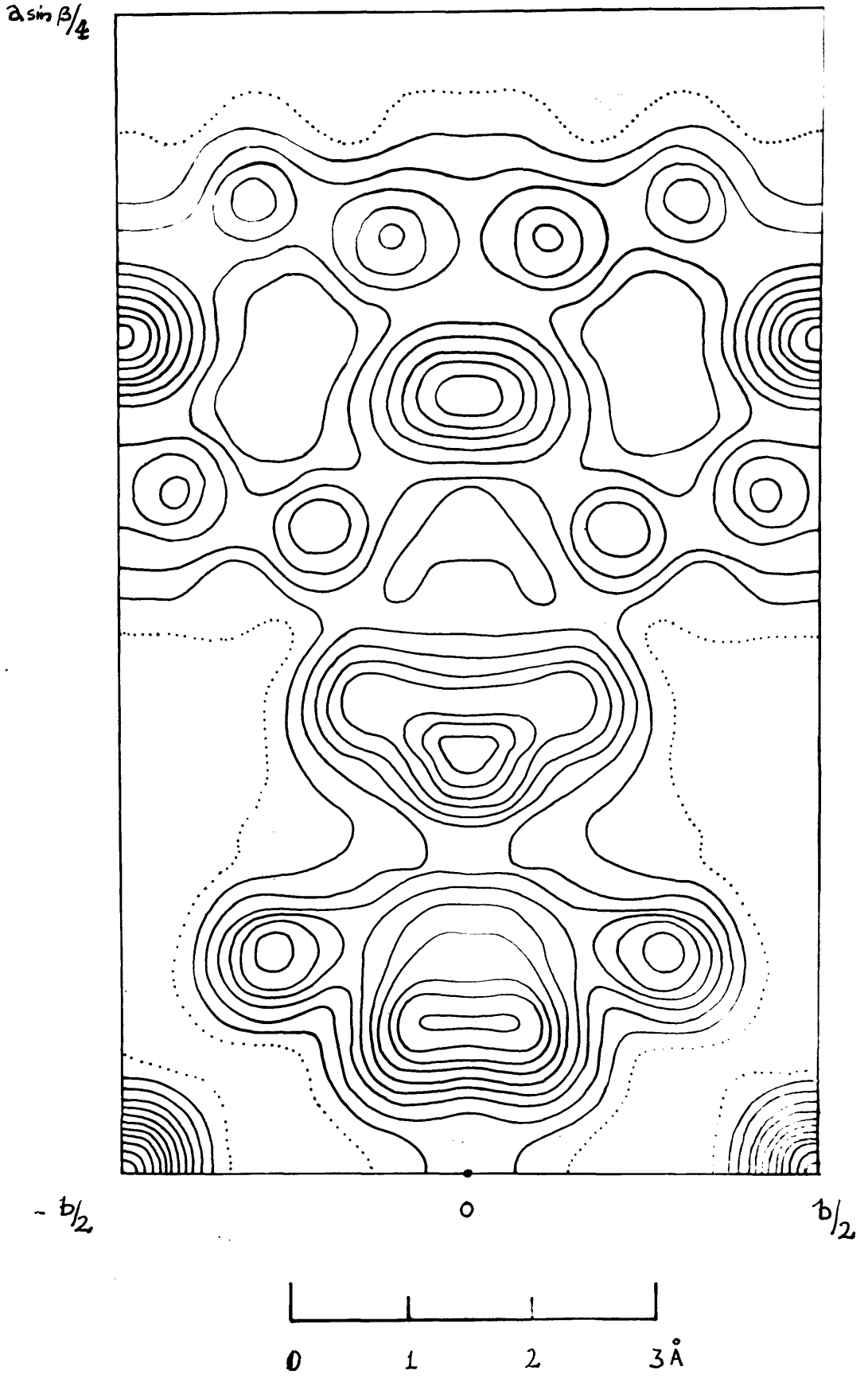
The contours represent increments in electron density of one electron / A^2, the one electron contour being dotted.

Fig. II. Projection of electron density for (hk0) for ammonium hydrogen di-cinnamate, showing the relationship between the two overlapping molecules.



The contours represent increments in electron density of one electron / A^2, the one electron contour being dotted.

0 1 2 3 Å


a sin β/4
- b/2
0
b/2
0
1
2
3 Å

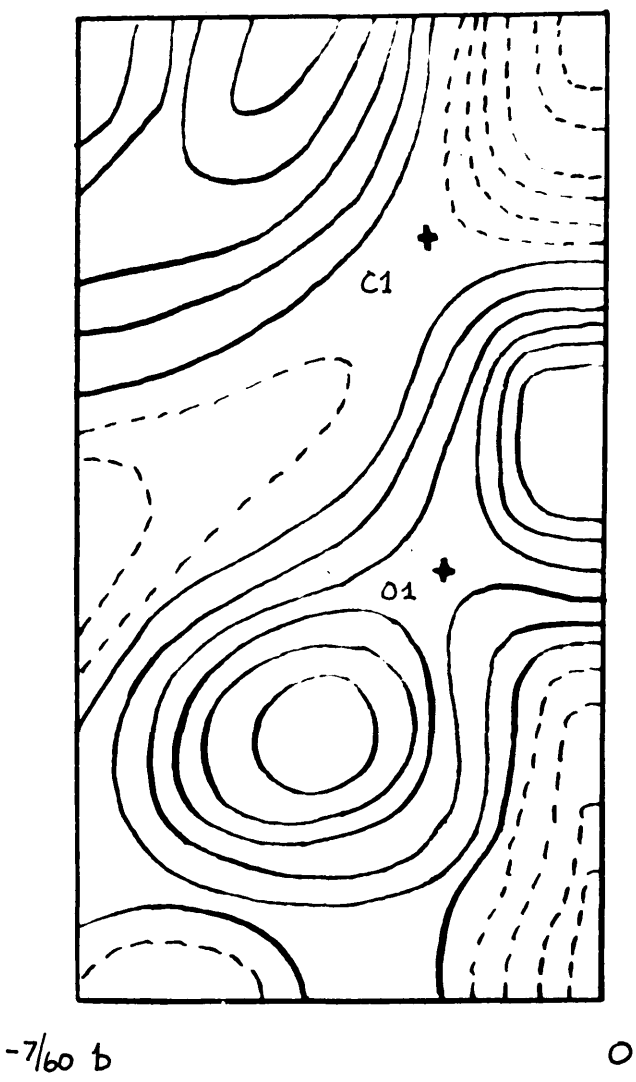


Fig. I2. Illustration showing residual electron density surrounding atoms O(I) and C(I). Contours represent increments of 0.2 electrons ; the negative areas being indicated by broken contours . The possible significance of these features is discussed in Appendix I to Part I.

correction of this nature applied would be of doubtful physical validity.

By lowering the value of B for the oxygen atoms to 4.4 the improvement in the structure factor agreement was sufficient to reduce R to a final value of I6.5 %. The exact significance of this step is discussed in Appendix I.

The final values for the atomic coordinates obtained from this projection are given below.

Atom	x/a	y/b
NH_4	0.0000	0.5000
O(I)	.0272	.I027
O(2)	.0469	- .2700
C(I)	.0528	- .0505
C(2)	.0902	-. 0476
C(3)	.I047	.I490
C(4)	.I400	.2I24
C(5)	.I478	.4I8I
C(6)	.I826	.4698
C(7)	.2II4	.309I
C(8)	.2026	.II32
C(9)	.I679	.0604

••••

The coordinates used to calculate bond lengths, bond angles and intermolecular approach distances etc., are given below. x/a, y/b, and z/c represent fractions of the cell edges, and X, Y, and Z give the coordinates in Angstrom units referred to orthogonal axes which are related to the cell axes as follows.

$$X = x\sin\beta$$
$$Y = y$$
$$Z = z - x\cos\beta \ .$$

The values of x/a taken are an average of the values obtained from the b and c axes projections.

Atom	x/a	y/b	z/c	X	Y	Z
NH_4	.0000	.5000	.2500	0.000	2.920	I.905
O(I)	.0280	.I027	.0543	I.056	0.470	0.3I6
O(2)	.0470	-.2700	.034I	I.772	-I.595	0.094
C(I)	.0527	-.0505	.0730	I.987	-0.350	0.369
C(2)	.0902	-.0476	.I396	3.40I	-0.278	0.738
C(3)	.I050	.I490	.I945	3.959	0.870	I.I0$
C(4)	.I398	.2I24	.2580	5.270	I.240	I.460
C(5)	.I476	.4I8I	.3509	5.565	2.442	2.I4I
C(6)	.I828	.4698	.4226	6.892	2.744	2.56I
C(7)	.2I07	.309I	.4068	7.943	I.805	2.342
C(8)	.2028	.II32	.3092	7.645	0.66I	I.624
C(9)	.I683	.0604	.24I7	6.345	0.353	I.234

The bond lengths and angles calculated from these figures are given in the diagram overleaf.

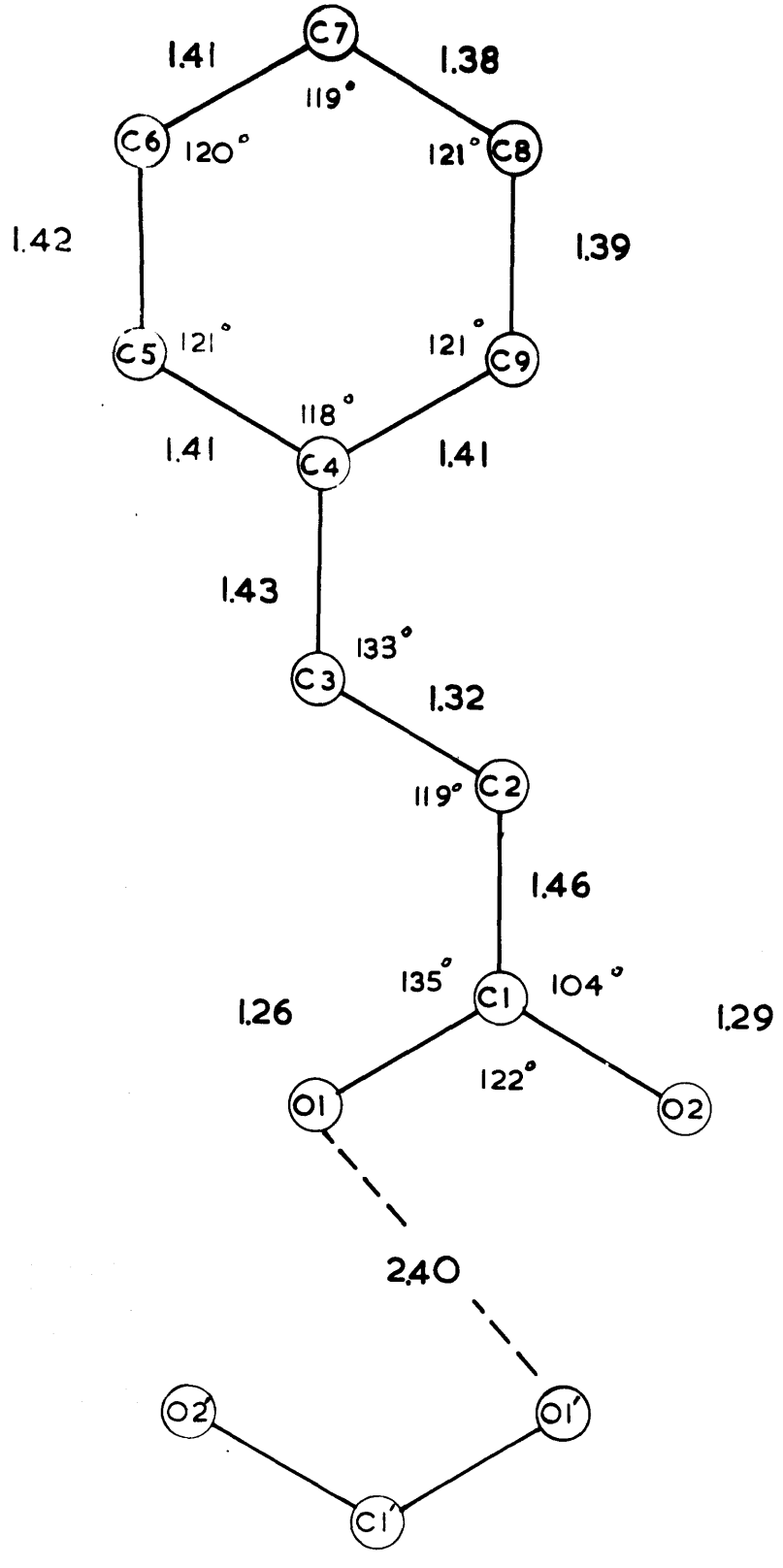


Fig. I3. Diagram illustrating the bond lengths (Angstrom units) and inter-bond angles found in ammonium hydrogen di-cinnamate.

Discussion of Results.

The bond lengths, bond angles, intra and inter-molecular approach distances etc. given in the diagrams above are discussed in this section.

The standard deviations (after Cruickshank) (viii), in atomic position are, for carbon :

$$\sigma(x) = 0.023 \text{ A.}$$
$$\sigma(y) = \sigma(z) = 0.020 \text{ A.}$$

and for oxygen :

$$\sigma(x) = 0.018 \text{ A.}$$
$$\sigma(y) = \sigma(z) = 0.016 \text{ A.}$$

Strictly these values only apply to the non-overlapped atoms and the error in the positions of particularly C(I) and O(I) is probably much greater, ca$\pm$0.05 A.

The minimum standard deviation in bond length is thus of the order of 0.03 A.

None of the bond length variations within the benzene ring are therefore significant, nor is any real difference in the C $\rightarrow$ O bonds probable.

The bond C(3) - C(4) is shortened significantly from the normal C - C single bond length of I.54 A. This can be put down to its being part of a conjugated system, as can also the shortening in the distance between C(I) - C(2).

The value of I33^{o} for the angle C(2)-C(3)-C(4), is in keeping with the values observed for such systems as stilbene,(ix) and the di-phenyl-polyenes (x).

The angles about the carboxyl group are of interest since a considerable distortion appears to have taken place. The group is planar, but the shortening of the bond C(I) - O(I) from a normal single bond separation, coupled with the increase in the volume of O(I) on ionisation would appear to have forced an increase in the angle O(I)-C(I)-C(2). The separation of 3.03 A. between O(I) and C(3) is comparable with that of 3.05 A. between C(2) and C(9).

By courtesy of Dr. T.R.R. McDonald(xi), an interesting comparison is possible between the bond lengths found for this salt, and those obtained by two-dimensional means for cinnamic acid. The largest variation occurs in the distance C(I) - C(2) which is in cinnamic acid I.50 A. The other relevant C - C distances agree to within $\pm$ 0.02 A. in each molecule. There is no distortion of the carboxyl group in the parent acid.

The atoms of the benzene ring are disposed about a mean plane whose equation, derived by the method of least squares , is :

$$x + 2.364y - 4.530z - 1.607 = 0$$

The average deviation of the atoms from this plane is 0.03 A. and the largest deviation is 0.12 A. in the case of C(3). The benzene ring is therefore effectively planar and although the deviation of C(3) from the mean plane is theoretically significant there is no valid reason why it should be so displaced and it seems likely that it will be coplanar with the benzene ring.

The side chain atoms C(I), C(2), and C(3) are disposed about the plane given by the equation :

$$x + 0.537\,y - 3.439\,z - 0.633 = 0$$

The average deviation from this plane is 0.017 A., and the greatest 0.030 A. These atoms are thus co-planar . The plane on which they lie makes an angle of 15° with the mean plane of the benzene ring atoms. This is probably due to steric repulsion between the hydrogen atoms which are attached to C(2) and to C(9) . This effect is observed in cinnamic acid, and in the other compounds referred to above (ix,x).

The atoms of the carboxyl group are also co-planar, the equation of their mean plane being :

$$x + 0.802\,y - 4.209\,z - 0.108 = 0,$$

the greatest deviation being 0.01 A. This plane effectively includes the origin, and it makes a small angle with the plane containing the side chain carbon atoms. The five atoms in question however are not co-planar as can be seen if an attempt is made to derive a mean plane through all five atoms, when deviations of up to 0.27 A. are found.

The shortest inter-molecular approach dist ance is between O(I) and O(I')., the hydrogen bond. It is unlikely that the true distance is as short as the observed value of 2.40 A., but the uncertainty in the position of O(I) prevents a more accurate determination by two-dimensional methods of analysis.

Each ammonium ion is surrounded by eight oxygen atoms four at 2.98 A. and four at 3.10 A. , the co-ordination being in the form of a tetragonal antiprism, as illustrated in the diagram overleaf. This is an uncommon arrangement in the acid salts, which apparently results from the siting of the ammonium ions exactly half way between two carboxyl groups at $y = \frac{1}{4}$, and $y = \frac{3}{4}$.

Fig. 14. Illustrating the arrangement of carboxyl groups about the ammonium ions. Atoms above the plane of the diagram are indicated by heavier circles.

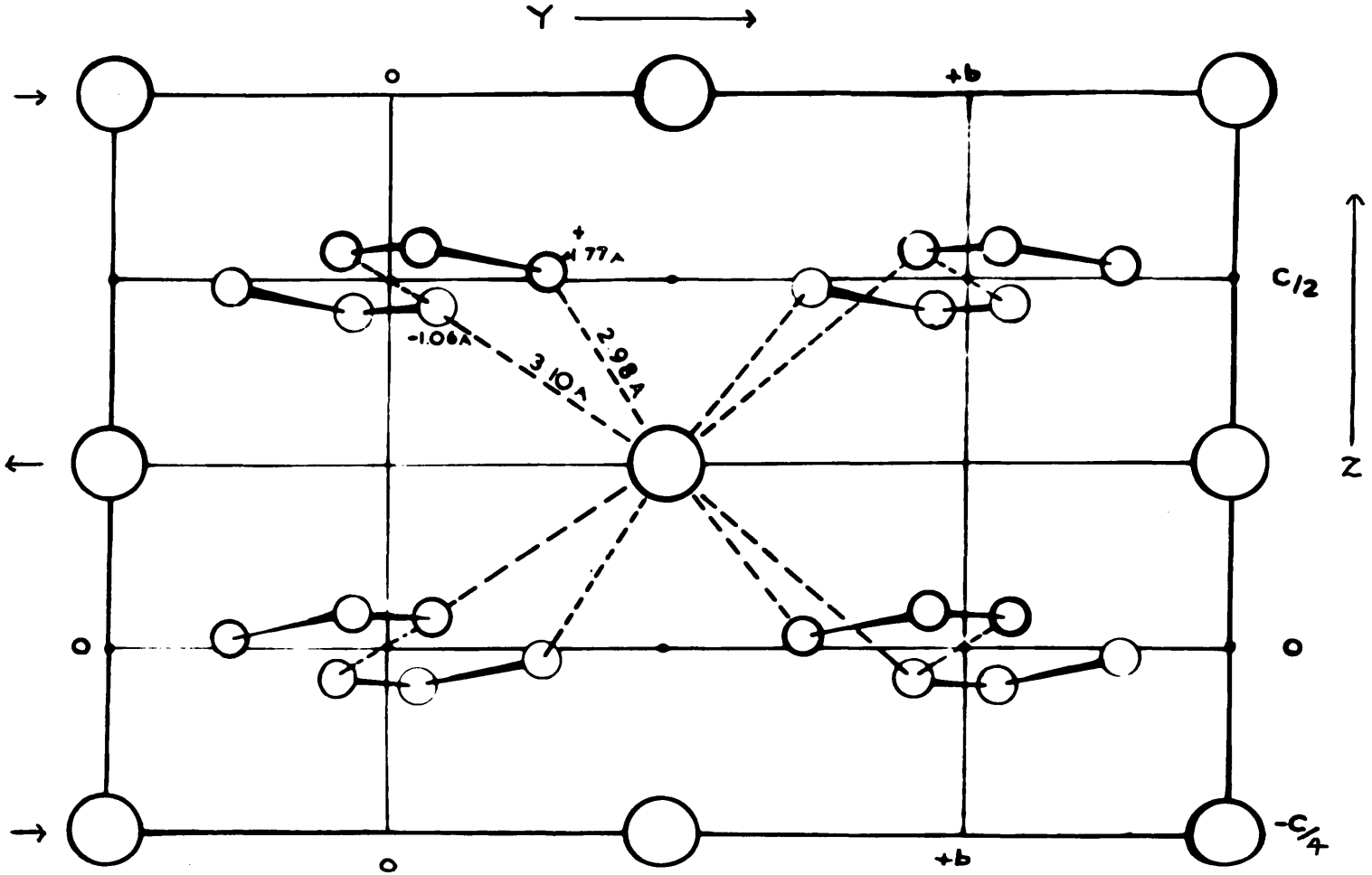


Table of inter-molecular approach distances in ammonium hydrogen di-cinnamate. With the exception of the distance O(I)...O(I'), which is between molecules x,y,z, and $\bar{x},\bar{y},\bar{z}$,; all contacts are between molecules x,y,z, and $x,\bar{\bar{y}},½ + z$.

O(I)...O(I')	2.40 A.
C(2)...C(I")	3.77 A.
C(3)...C(2")	3.54 A.
C(8)...C(9")	3.79 A.
C(7)...C(8")	3.97 A.

All other distances are in excess of 3.8I A. and in common with other acid salts of this type the structure is a very open one.

References : Part One, Section Three.

i. P. Carrick : J. fur Prakt. Chimie, (2),45, 514.

ii. W.J.C. Wilson : Acta Cryst.,(1949),2, 318.

iii. E.R. Howells, D.C. Phillips, D. Rogers : ibid(1950),3, 210.

iv. A.J.C. Wilson : Nature, (1942), 150, 152.

v. G. Albrecht : Rev. Sci. Instr., (1939) 10, 221.

vi. R. McWeeny : Acta Cryst. (1951), 4, 513.

vii. J.C. Speakman et al. : J. (1949), 3357.
J. (1951), 185.
J. (1954), 180.
loc.cit., 787.

viii. D.W.J. Cruickshank : Acta Cryst.,2, 65.

ix. J.M. Robertson, I. Woodward : Proc. Roy. Soc.,A, 162, 568.

x. W. Drenth, E.H. Wiebenga,: Acta Cryst., (1955),8, 755

xi. T.R.R. McDonald : personal communication.

Appendix One to Part One, Section Three.

Notes on the scattering functions used in the calculation of structure factors in ammonium hydrogen di-cinnamate.

When work on this salt was begun no entirely satisfactory scattering function had been derived for the ammonium ion. In ammonium hydrogen di-salicylate the scattering function used was the James and Brindley curve for oxygen (i), which was modified in the later stages of the analysis by a method similar to that of Luzatti (ii). This gave a fairly satisfactory empirical function, which is however inadequate in that it only allows for seven electrons associated with the ammonium ion instead of the more likely ten.

Since each ammonium ion in the present case has eight almost equi-distant nearest neighbours, it is unlikely that the hydrogen atoms are involved in any type of hydrogen bonding. and the whole ion was therefore treated as a single scattering unit, by assuming three extra electrons to be present distributed among the outer orbitals.

The scattering curve was originated at f = IO, with ζ (2.sinθ), = O., and by ζ = I.OO was reduced to the normal McWeeny curve for a simple nitrogen atom.

From the appearance of the (F_o - F_c) maps this arrangement seems to have been entirely satisfactory since no indication of any significant residual electron density within a radius of I.6 A. of the position of the ion was found.

Around the oxygen atom O(I), involved in the hydrogen

bond there persists in the final (F_o - F_c) maps for (hkO) peculiar distribution of electron density which is shown in Figure I2.

Various interpretations of this feature are possible. Firstly it may be due to either random or systematic errors in F_o s.

Secondly it may be assumed to represent some form of anisotropic vibration of the oxygen atom about its mean position. The corresponding maps for (hOl) are not helpful in deciding this point , and an acceptance of this view implies that the motion has a substantial component in the direction of the bond O(I) - C(I), which is not very likely.

In deriving a scattering function forthe oxygen atom which would take account of the extra half electron associated with each oxygen atom, (assuming the charge to be uniformly distributed), the James and Brindley curve for oxygen had been multiplied by a factor of 8.5/8.0, in previous analyses in the series, and the Mc Weemy curve for oxygen (valence states), had been similarly treated in this analysis.

It is not now altogether certain that this represents a good approximation to the physical state of the oxygen ion since it implies that the distribution of scattering matter remains unchanged and that every electron is given a scattering power equivalent to 8.5/8.0 e.

The temperature factor B derived for oxygen by Wilson's method (iii) was 3.8, and this subsequently had to be increased to 6.3 to accomodate the (F_o - F_c) data, as compared to a value of 5.5 for carbon. It is thus possible that the temperature factor has become artificially high in order to

compensate for an excessive scattering due to this method of weighting, and it seems possible that a curve based on similar considerations as that for the ammonium ion should have been used.

This view is supported by the improvement in the agreement between F_o and F_c which results, if a McWeeny curve for oxygen with a value of $B = 4.0$ is used, in the higher ranges of ζ. In the lower ranges of ζ however the agreement deteriorates to an extent which outweighs this, and it may be that the peculiar appearance of the $(F_o - F_c)$ maps is due to an inappropriate scattering curve having been used, which adversely affects the agreement between F_o and F_c at certain ranges of ζ .

References

i. R.W. James, G.W. Brindley : Zeit.f.Krist.,(1931), 78, 470.

ii. V. Luzzati : Acta Cryst.,(1953), 6, 158.

iii. A.J.C. Wilson : Nature, 150, 152.

Table of observed structure amplitudes and calculated structure factors for (hol) ammonium hydrogen di-cinnamate.

h00				h02			
Index	ζ	Fo	Fc	Index	ζ	Fo	Fc
2	0.083	49.5	+ 44.9	0	0.405	34.8	- 26.6
4	.I65	I9.9	- 2I.3	2	.4I5	60.9	+ 62.3
6	.247	I00.4	+ 94.3	4	.430	9I.7	- 83.I
8	.350	70.5	- 7I.8	6	.487	46.7	- 38.8
I0	.4I2	5.3	+ 7.8	8	.540	90.7	- 99.4
I2	.495	59.5	- 59.9	I0	.600	53.0	- 64.0
I4	.570	24.9	- I9.I	I2	.660	I02.9	-I03.9
I6	.658	5I.2	- 47.3	I4	.726	76.I	- 84.4
I8	.74I	3.2	- 2.0	I6	.796	66.2	+ 5I.3
20	.825	60.6	+ 58.I	I8	.867	3.3	+ 4.0
22	.906	34.8	+ 3I.I	20	.945	3.3	- 3.9
24	.990	II.3	+ 6.0	22	I.0I9	I3.2	+ 8.4
26	I.07I	2I.6	- 29.4	24	I.097	7.9	- 9.I
30	I.I55	I5.5	+ I4.7	26	I.I74	3.3	- 5.8
32	I.237	I.8	- 4.2	28	I.252	I5.9	- 7.3
32	I.320	I4.5	- 2I.I	30	I.323	8.6	- 6.0
34	I.404	I4.6	+ I7.4	32	I.4II	3.3	+ 5.0
36	I.485	2.3	+ 4.4	34	I.488	4.3	+ 7.4
38	I.568	4.2	+ 8.4	36	I.569	3.3	+ 3.4
40	I.650	3.9	+ 5.3	38	I.650	3.3	+ 3.2
42	I.73I	3.6	+ 5.4	40	I.728	3.3	+ 2.4

Index	ζ	$\bar{h}02$ F_o	F_c
2	0.405	94.0	+ 92.0
4	.424	300.0	+304.7
6	.457	48.3	- 46.4
8	.502	68.8	- 72.2
I0	.553	63.9	- 65.3
I2	.6II	34.I	- 42.9
I4	.677	35.7	- 35.8
I6	.744	54.6	- 62.8
I8	.8I4	I6.2	- I9.3
20	.888	28.8	- 25.6
22	.962	6.6	+ 7.7
24	I.039	9.9	+ 9.8
26	I.II5	I8.9	+ I5.3
28	I.I9I	I7.2	- I8.I
30	I.275	42.0	- 43.0
32	I.350	25.5	+ I8.6
34	I.429	I2.9	- I2.3
36	I.5I0	I0.6	- I0.4
38	I.587	I7.2	+ I6.8
40	I.670	3.3	- 3.3
42	I.750	3.3	+ 4.8
44	I.826	3.3	+ 0.8
		h04	
0	0.806	I8.2	+ I9.9
2	.8I5	22.8	+ I7.4
4	.824	27.I	- 28.I
6	.864	7.3	- I7.6
8	.89I	38.4	- 48.6
I0	.933	52.3	- 54.4

Index	ζ	h04 F_o	F_c
I2	.972	4I.0	+ 26.8
I4	I.025	I7.2	+ 8.3
I6	I.069	3.3	+ 5.4
I8	I.I36	34.4	+ 3I.I
20	I.I95	3.3	+ 4.6
22	I.260	3.3	+ 2.2
24	I.322	I2.0	+ I3.8
26	I.388	I4.9	+ 9.8
28	I.458	-	-
30	I.53I	I7.9	+ I6.9
32	I.600	4.3	- 5.2
34	I.67I	3.3	+ 2.7
		$\bar{h}04$	
2	0.807	23.4	- 3I.8
4	.8I2	6I.9	+ 6I.I
6	.825	72,4	+ 86.4
8	.850	67.7	+ 7I.9
I0	.879	4.4	+ I2.8
I2	.9I4	3I.8	- 3I.I
I4	.955	40.5	- 34.4
I6	I.004	27.4	+25.7
I8	I.053	I2.8	- 4.2
20	I.II0	I4.2	- I4.I
22	I.I66	I5.9	+ II.0
24	I.230	2.9	+ 0.I
26	I.292	I4.2	+ I3.5
28	I.357	9.3	+ 4.0
30	I.430	I0.I	+ 9.I
32	I.495	I5.0	- I6.0

$\bar{h}04$

Index	ζ	F_o	F_c
32	I.495	I5.0	- I6.0
34	I.565	I3.3	- I9.I
36	I.636	I4.5	+ I5.6
38	I.707	2.9	- 2.9
40	I.780	-	-
42	I.854	3.3	+ 2.7

h06

0	I.2I2	24.4	- 2I.5
2	I.2I6	2.6	- I0.3
4	I.233	I7.5	- 25.2
6	I.254	30.3	+ 29.4
8	I.278	2.6	- I2.2
I0 to 22,0,6	absent reflexions		
24	I.622	2.6	+ 2.I
26	I.678	9.3	+ I2.5
28	I.736	2.6	- 6.0
30	I.800	6.7	- 3.6

$\bar{h}06$

2	I.208	I2.I	+ I2.6
4	I.2II	-	-
6	I.2I5	8.5	- 8.2
8	I.230	30.I	+ 30.0
I0	I.246	20.8	+ I8.I
I2	I.270	2.6	- I.I
I4	I.297	2.6	- I.6
I6	I.330	3I.4	- 26.0
I8	I.365	I9.8	- I4.3

$\bar{h}06$

Index	ζ	F_o	F_c
20	I.409	II.6	+ I5.0
22	I.453	5.7	- 5.5
24	I.503	2.6	- 6.0
26	I.552	3.6	+ 2.2
28	I.604	3.3	- 3.7
30	I.664	I2.6	- 3.I
32	I.722	3.I	- I.0

h08

0	I.6I4	3.I	- 2.9
2	620	3.I	- 4.5
4	I.635	3.I	- 6.8
6	I.650	3.I	- 4.8
8	I.670	II.I	+ II.8
I0	I.696	4.6	+ 5.3
I2	I.723	5.2	+ 8.9
I4	I.755	II.4	+ 8.9
I6	I.790	3.I	+ 2.8

$\bar{h}08$

2	I.6I3	3.I	- 2.9
4	I.6I3	4.I	- 6.0
6	I.6I6	I6.0	+ I2.9
8	I.624	3.I	+ 3.4
I0	I.638	3.I	- 2.0
I2	I.653	I4.I	+ I5.0
I4	I.672	4.0	+ 5.5
I6	I.695	3.7	+ 0.7
I8	I.723	3.7	- 2.6
20	I.756	4.3	- 4.7
22	I.790	3.I	+ I.4
24	I.830	4.3	+ 6.I

Table of structure factors for (hk0) for ammonium hydrogen di-cinnamate.

h00				hI0			
Index	ζ	F_o	F_c	Index	ζ	F_o	F_c
2	0.083	49.5	+ 47.3	I	0.275	I0I.2	+ 94.9
4	.I65	I9.9	- I7.4	3	.295	I7.8	+ 22.5
6	.247	I00.4	+I00.8	5	.340	45.5	- 40.6
8	.350	70.5	- 64.7	7	.400	63.6	- 72.2
I0	.4I2	5.3	+ 7.8	9	.467	I4.3	- I4.9
I2	.495	59.5	+ 53.5	II	.520	II.5	- 5.7
I4	.570	24.9	- 2I.I	I3	.604	40.8	- 46.6
I6	.658	5I.2	- 50.4	I5	.680	72.0	- 68.6
I8	.74I	3.2	- 5.8	I7	.750	38.7	- 38.4
20	.825	60.6	+ 6I.8	I9	.838	4.4	+ 2.9
22	.906	34.8	+ 27.8	2I	.9I2	24.5	- 26.6
24	.990	II.3	+ 9.5	23	I.000	2.7	- 0.3
26	I.07I	2I.6	- 27.4	25	I.074	2.7	- 0.5
28	I.I55	I5.5	+ I2.6	27	I.I55	33.8	- 37.I
30	I.237	I.8	+ 2.0	29	I.236	9.2	+ 8.6
32	I.320	I4.5	- I6.7	3I	I.3I5	9.0	+ I0.7
34	I.404	I4.6	+ I4.2	33	I.396	5.9	- 8.5
36	I.485	2.3	+ 4.7	35	I.466	I6.7	+ I8.I
38	I.568	4.2	+ 7.4	37	I.560	2.9	+ I.5
40	I.650	3.9	+ 5.7	39	I.640	I.8	- 0.8
42	I.73I	3.6	+ 6.6	4I	I.7I6	I.I	- 2.0
				43	I.777	-	-
				45	I.885	I.5	- I.0

h20

Index	ζ	F_o	F_c
0	0.540	73.4	+ 67.5
2	.547	7.6	+ I4.7
4	.570	6.3	+ 5.5
6	.595	53.5	+ 53.9
8	.632	7.6	- 9.6
I0	.680	32.2	+ 36.9
I2	.730	58.2	+ 72.6
I4	.792	33.8	- 2I.I
I6	.862	4.4	+ 5.5
I8	.932	2.4	- 7.8
20	.992	25.3	- 2I.2
22			
24			
26	I.2I0	4.8	+ 2.3
28	I.285	4.0	- 4.2
30	I.350	5.2	+ 4.2
32	I.440	I6.7	+ I6.I
34	I.5I0	I8.7	+ I7.5
36	I.584	2.I	+ 2.2
38	I.666	I.2	- 0.7
40	I.740	-	-
42	I.8I2	3.9	- 3.0

h30

Index	ζ	F_o	F_c
I	0.808	I.I	- 2.2
3	.820	I6.8	+ I6.7
5	.844	I.5	+ I.3
7	.862	35.4	- 37.4

h30

Index	ζ	F_o	F_c
9	0.894	I9.0	- 25.7
II	.936	26.6	- 24.0
I3	.978	I.I	+ 4.2
I5	I.020	I7.6	- I4.8
I7	I.073	5.2	- 7.9
I9	I.I28	3.7	+ 9.7
2I	I.I90	5.5	- I3.0
23	I.250	I6.2	+ I5.8
25	I.3I6	9.4	+ 6.2
27	I.380	7.8	- I5.0
29	I.452	6.6	- 9.9
3I	I.5I6	I.2	- 4.6
33	I.58I	I.2	+ 2.6

h40

Index	ζ	F_o	F_c
0	I.074	2.2	+ I0.5
2	I.080	6.9	+ II.3
4	I.089	-	-
6	I.I00	-	-
8	I.II4	2.3	- 9.I
I0	I.I46	-	-
I2	I.I84	6.4	+ 8.6
I4	I.225	7.2	+ 6.6
I6	I.272	7.I	+ I3.2
I8	I.324	6.6	+ 9.0
20	I.364	6.6	+ I.I
22	I.4I4	26.7	+ 24.3
24	I.470	I0.0	+ 7.8
28	I.584	2.3	+ 2.I

h50

Index	ζ	F_o	F_c
I	I.348	I0.2	- I5.5
3	I.352	I2.0	- II.4
5	I.360	22.0	- 22.I
7	I.378	I4.2	+ I6.7
9	I.394	I.9	- 3.I
II	I.420	-	-
I3	I.452	7.4	+ I2.3
I5	I.478	-	-
I7	I.5I8	2.5	- 0.8
I9	I.564	2.5	- 5.8
2I	I.600	5.6	+ 6.2
23	I.648	5.2	- 4.8
25	I.752	2.2	- 4.6
	h60		
6	I.632	3.0	- 3.2
8	I.648	2.0	- 3.7
I0	I.666	9.0	+ I3.0
I6	I.744	3.0	+ 3.9
I8	I.784	5.0	+ 2.8

PART TWO

SECTION ONE

The unit cell dimensions of some para-alkoxybenzoic acids.

Introductory

The series of para-alkoxy benzoic acids is of interest structurally, because of the ability of the members of the series to show liquid-crystalline behaviour on melting.

The first observations on the series were made by A.E. Bradfield and Brynmor Jones (i), for the para-propoxy, and para-butoxybenzoic acids, and these were extended by Brynmor Jones (ii), and later by G.M. Bennett and Jones (iii), who extended the study to cover the acids in the series up to and including para-cetyloxybenzoic acid. They showed the existence of a nematic phase in those acids between the para-propoxy and para-hexyloxy acids, and of both a smectic and a nematic phase in the higher acids.

Though neither para-methoxy nor para-ethoxybenzoic acid independently show this behaviour, a melt of the two acids does, showing that it is the high melting points of these acids which inhibits the formation of a nematic phase.

Bennett and Jones claimed that para-propoxybenzoic acid was the simplest molecular structure to exhibit such mesomorphism, and suggested a dimeric arrangement of two molecules of the acid, of a type which has since become extremely familiar in carboxylic acids.

This claim has been disputed by Weygand and Gabler (iv), in favour of para-n-butylbenzoic acid, of essentially similar basic structure, though without the polar group sometimes thought to be an essential feature of such nematic substances.

Some connection between the crystal structure and the mesomorphism of these acids would be of interest, and this present investigation has been undertaken with a view to examining this point.

Preliminary crystal data have been collected for the members of the series up to para-nonyloxybenzoic acid, and are given below. The structure of para-methoxybenzoic acid has been elucidated in detail, and that of para-ethoxybenzoic acid in single projection, and these are described in Sections two and three respectively.

Crystal Data

para-methoxybenzoic acid :

$a = 16.87$, $b = 10.99$, $c = 4.00$ A. $\beta = 95.8^{\circ}$

Monoclinic, $P2_1/a$.

para-ethoxybenzoic acid :

$a = 22.04$, $b = 4.01$, $c = 9.51$ A. $\beta = 98^{\circ}$

Monoclinic, $P2_1/a$.

para-propoxybenzoic acid :

$a = 15.52$, $b = 7.52$, $c = 8.00$ A. $\beta = 94^{\circ}45'$

Monoclinic, $P2_1/c$.

para-butoxybenzoic acid :

$a = 16.95$, $b = 7.76$, $c = 9.64$ A.

Monoclinic.

para-amyloxybenzoic acid :

a = 15.95, b = 7.30, c = 10.0 A. β = 102°

Monoclinic , $P2_1/m$.

para-hexyloxybenzoic acid :

The data for this acid have been rejected owing to the high, but unconfirmed, likelihood of twinning in all crystals available. Presumptively monoclinic.

para-heptyloxybenzoic acid :

a = 7.86, b = 4.88, c = 17.99 A.

α = 88° β = 100° γ = 102°

Triclinic : P I, or P $\bar{1}$.

para-octyloxybenzoic acid :

a = 7.88, b = 4.9 c = 19.3 A.

α = 88° β = 100° γ = 101°

Triclinic ; P I, or P $\bar{1}$.

para-nonyloxybenzoic acid :

a = 7.9, b = 4.9, c = 21.76 A.

α = 88° β = 98° γ = 103°

Triclinic : P I, or P $\bar{1}$.

It is unwise to base any dogmatic conclusions with regard to molecular and crystal structure on the evidence of cell dimensions alone, but it is perhaps permissible to comment on the similarity of the cell constants from para-heptyloxybenzoic acid onwards.

It is evident from Weissenberg photographs of these acids that the structures of the para-heptyloxy, and para-nonyloxy are very closely similar. That of the para-octyloxy acid is also closely related to these two, but, presumably because the side chain contains an odd number of atoms, is not quite the same.

The 'a' and 'b' dimensions of all three are closely similar to the corresponding dimensions of the orthorhombic sub-cell found in the normal straight chain fatty acids with triclinic space group, which are given by von Sydow (v), as (average values) 4.96, and 7.77 A. Thus as the side chain in the acids becomes of dominant importance it may be assumed that the structure is becoming more like that of the corresponding normal fatty acid.

It is with heptyloxybenzoic acid that the smectic phase is first observed, and with this acid also ,and the higher members of the series more than one solid phase is found, which is also reminiscent of the behaviour of the normal fatty acids. (vi).

About the acids from para-propoxy to para-hexyloxy it is difficult to draw any conclusions at the present stage, but these substances do offer an attractive prospect from a structural point of view, particularly with the effectiveness of the Fourier transform method of phase determination so well established in the case of the para-ethoxybenzoic acid.

References : Part Two, Section One.

(i) A.E. Bradfield, B. Jones : J.,(I929), 2660.

(ii) B. Jones : J.,(I935), I874.

(iii) G.M. Bennett, B. Jones : J.,(I939), 420.

(iv) A. Weygand, P. Gabler : Z.phys.Chem. B 46, 270.

(v) E. von Sydow : Arkiv f.Kemi. (I956),9,23I.

(vi) E. Stenhagen, E. von Sydow : ibid,(I953), 6, 309.

PART TWO

SECTION TWO

The Crystal and Molecular Structure of para-methoxybenzoic acid.

para-Methoxybenzoic Acid.

Introductory.

The morphology of para-methoxybenzoic acid, or anisic acid, is given in Groth, IV, 504, where it is stated to be monoclinic with $\beta = 98^{\circ}26'$, and with the axial ratio :

I.5497 : I.0000 : 0.3615 .

The unit-cell dimensions have been measured by Rokade and his collaborators (i), who confirm the monoclinic symmetry and give the cell dimensions :

$a = 16.82$, $b = 10.94$, $c = 3.95$, $\beta = 94^{\circ}54'$.

From systematic absences on oscillation photographs they conclude the space group to be $P2_1/a$.

This analysis was begun by T. Downie and T. Palmer (ii) working in Glasgow, who took some initial photographs and produced a reasonable trial structure for the c axis projection. Photographs taken by them seemed to indicate that the acid possessed a space group of orthorhombic symmetry, with the presence of three mutually perpendicular symmetry planes apparently established from oscillation photographs. The cell dimensions found by them were in fair accord with those given by Rokade.

Under the polarising microscope however crystals of anisic acid grown from methanol solution showed oblique extinction, in a direction at 18° to the needle axis of the crystal. This fact, apparently overlooked by Downie and Palmer excludes the possibility of orthorhombic symmetry. The plane of symmetry found by these two workers

on oscillation films taken about the needle axis must therefore be due either to their having used a polymorphic form of anisic acid, or more likely, to their having used a twinned crystal in that particular experiment.

This latter alternative was proved correct when after scrutiny, a twinned crystal of the type illustrated was found in a batch of crystals grown from methanol solution under conditions of controlled evaporation. The large specimen found showed clearly the presence of the re-entrant angles associated with this type of twinning, and under the polarising microscope showed two directions of extinction inclined at 36° to one another. Oscillated through 15° about the needle axis, X - ray photographs could be taken which showed the spurious symmetry.

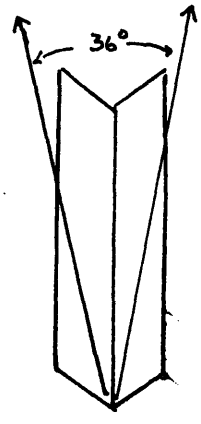


Fig. 14a. Showing type of twinning found in anisic acid crystal.

Cell Dimensions and Crystal Data.

The cell dimensions were confirmed by rotation photographs taken, using Copper K_{α} radiation (λ = I.542 A.), about the three principle axes. The space group symmetry and the angle β were deduced from Weissenberg photographs taken about (OIO) and (OOI) . The results are summarised, together with other relevant data , in the table overleaf.

Table of Crystal Data for para-methoxybenzoic acid.

$CH_3O.C_6H_4.COOH$ M = I52 F(000) = 320 m = I84°

Monoclinic prismatic.

a = I6.87 (± .05)
b = I0.99 (± .04)
c = 4.00 (± .02) A.
β = 95.8°

Volume of unit cell = 737.9 A^3.

ρ observed = I.364 ; calculated on the basis of four molecules per unit cell, ρ = I.360.

Systematic absences : (h0l); when h = 2n+I
(0k0); when k = 2n+I.

Space group : $P2_1/a$, (C_{2h}^5).

Collection of Intensity Data.

For the collection of intensity data, use was made of the Robertson Multiple Film Technique (iii) using a pack of five films. Intensity data had been collected for (hk0) , and this was duplicated for checking purposes. Data was also collected for (h0l). In (hk0) I08 out of a possible I30 reflections had been recorded, and in (h0l) 54 out of a theoretically accessible 92. This gives a ratio of positional parameters to reflections of about I:5 in(hk0) and I:2.5 in (h0l).

Since the crystal habit is approximately cylindrical, no corrections for absorption were applied. In one instance a low order reflection ,(020), appears to be affected by secondary extinction, and this was allowed for in later

syntheses by including this term at its calculated value.

Structure amplitudes were derived in the usual manner, and these were placed on an absolute scale by the use of Wilson's method (iv), and later by comparison with the calculated values of the structure factors.

Tables of intensity data are given as an appendix .

Structural Work : The c axis projection.

The c axis of the crystal is agreeably short, and a good representation of the electron density would be expected from a projection down this axis. Palmer had derived a promising trial structure by trial and error methods based on a few strong reflections from this zone. This structure was used as the basis for further refinement.

New atomic centres were chosen from Palmer's last projection and structure factors were calculated for all planes.

The structure factor expression for (hk0) is given by

$$A = 4f.\Sigma \cos 2\pi hx.\cos 2\pi ky \quad \text{where } h + k = 2n.$$

$$A = -4f.\Sigma \sin 2\pi hx.\sin 2\pi ky \quad \text{where } h + k = 2n + I.$$

The scattering functions, f , used were the McWeeny functions for carbon and oxygen, valence states, modified by an isotropic temerature factor B of 2.8 .(v)

This calculation enabled the phase constants associated with 99 of the observed structure amplitudes to be determined. These 99 terms were used as coefficients in a

double Fourier series, computed at 6° intervals along each axis; (0.281 A. along a, and 0.183 A. along b).
The electron density for the (hk0) projection is given by the expression :

$$P(hk0) = \frac{1}{A}\left[F(000) + 2\left\{ \sum_{2}^{\infty} F(h00)\cos 2\pi hx + \sum_{2}^{\infty} F(0k0)\cos 2\pi ky \right\} + 4\left\{ \sum_{1}^{\infty}\sum_{1}^{\infty} F(hk0)\cos 2\pi hx \cdot \cos 2\pi ky - \sum_{1}^{\infty}\sum_{1}^{\infty} F(hk0)\sin 2\pi hx \cdot \sin 2\pi ky \right\} \right]$$

(with $h+k=2n$ for the double summations).

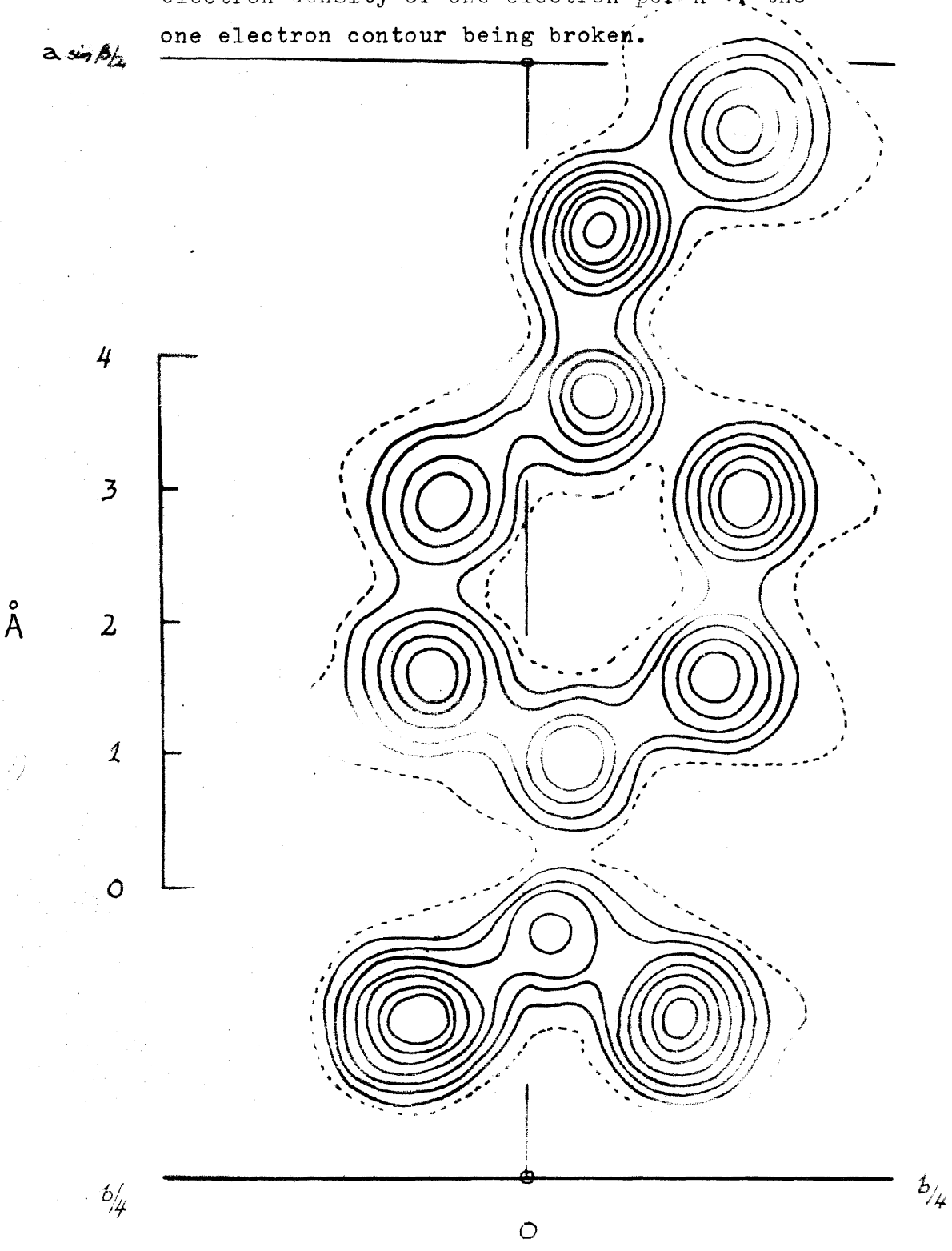
An electron density map based on this summation showed good resolution of all atoms. New atomic centres were chosen and the structure factor calculation repeated. This gave a value for R in the usual terms of 29 % . A further cycle of refinement of this nature led to the electron density projection illustrated overleaf, which includes all 108 terms available. The value of R at this stage was 23 % .

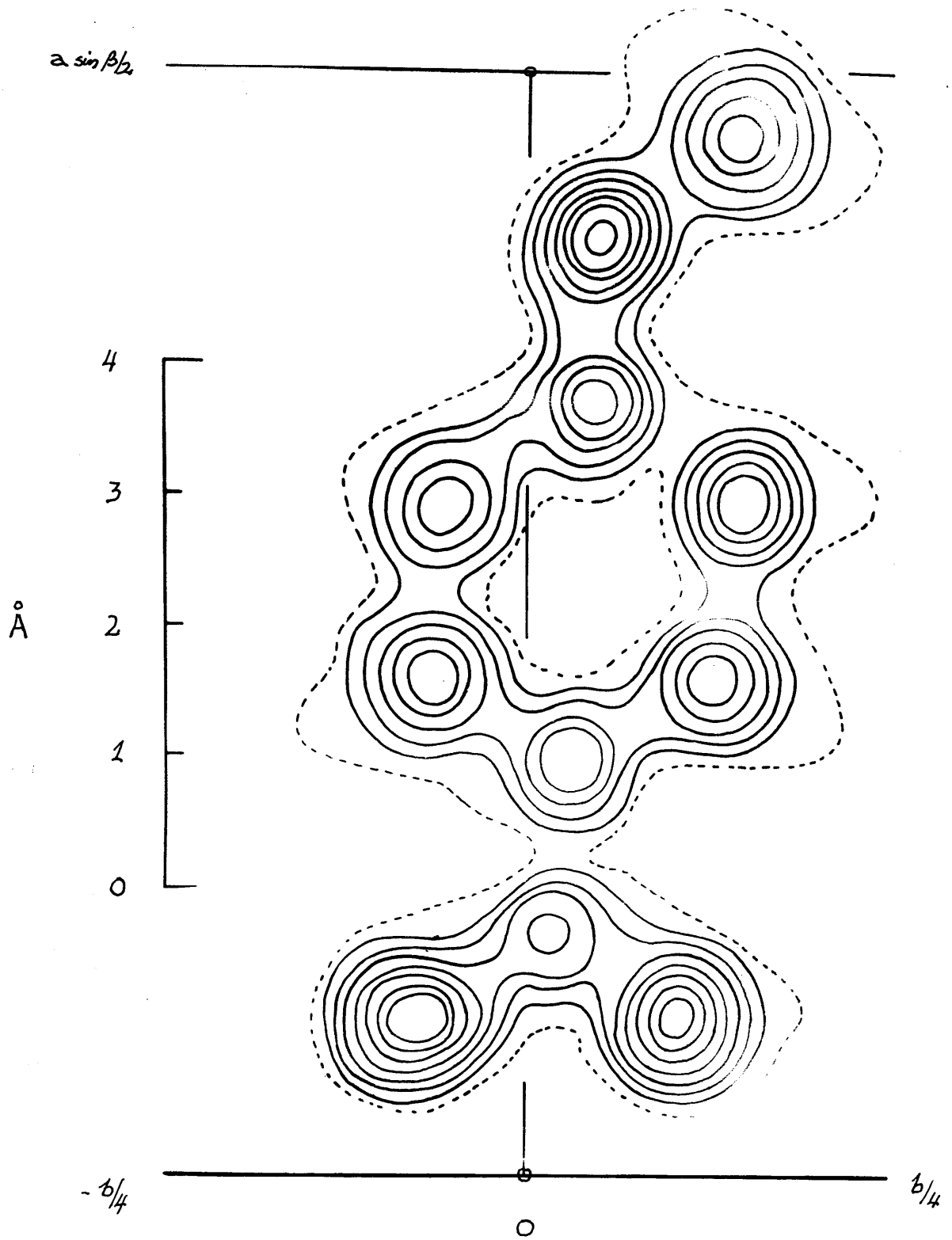
To further the refinement it was decided to use (F_o - F_c) syntheses, since all the atoms in this projection are well resolved and offer an ideal situation for the application of this method of refinement. Allowance was made for the hydrogen atoms attached to the benzene ring by placing them at distances corresponding to C - H bond lengths of I.I A. in projection. No allowance was made for the methyl hydrogen atoms, nor was it possible at this point to assign a likely position to the carboxyl hydrogen atom since the carbon - oxygen bonds remained undifferentiated.

As a result of the first difference synthesis several shifts were made in atomic positions so as to minimise tthe gradients at these points ; it was possible to assign a

Fig. I5. Projection of electron density for (hkO) for anisic acid. Contours represent increments in electron density of one electron per A^2 , the one electron contour being broken.

Fig. I5. Projection of electron density for (hkO) for anisic acid. Contours represent increments in electron density of one electron per A^2, the one electron contour being broken.




a sin β/2
4
3
Å
2
1
0
- b/4
b/4
0

likely site to the carboxyl hydrogen atom, and suitable positions to two of the methyl hydrogens. Calculation of structure factors embodying these alterations gave a good improvement in the agreement. Two further syntheses and structure factor calculation gave a value of R = 12.8% (10.6% if (020) is included at its calculated value) at which stage the observed and calculated data were held to be sufficiently attuned.

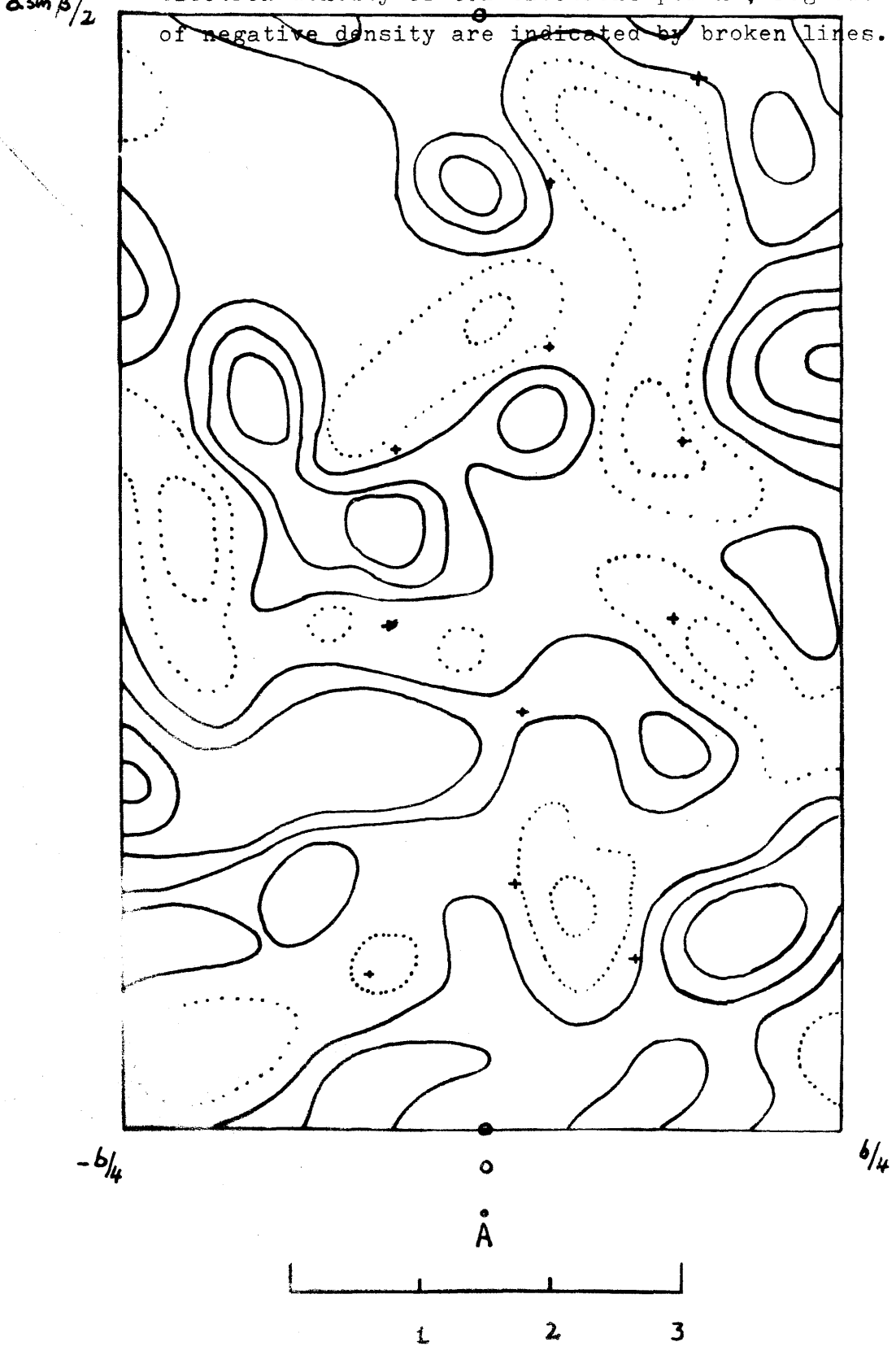
Throughout the refinement the value of the temperature factor B remained constant nor was there any convincing evidence of any anisotropic thermal motion associated either with the molecule as a whole, or with any atom in particular. The final residual electron density projection for this zone is illustrated overleaf. The final values of the coordinates derived from this projection are tabled below.

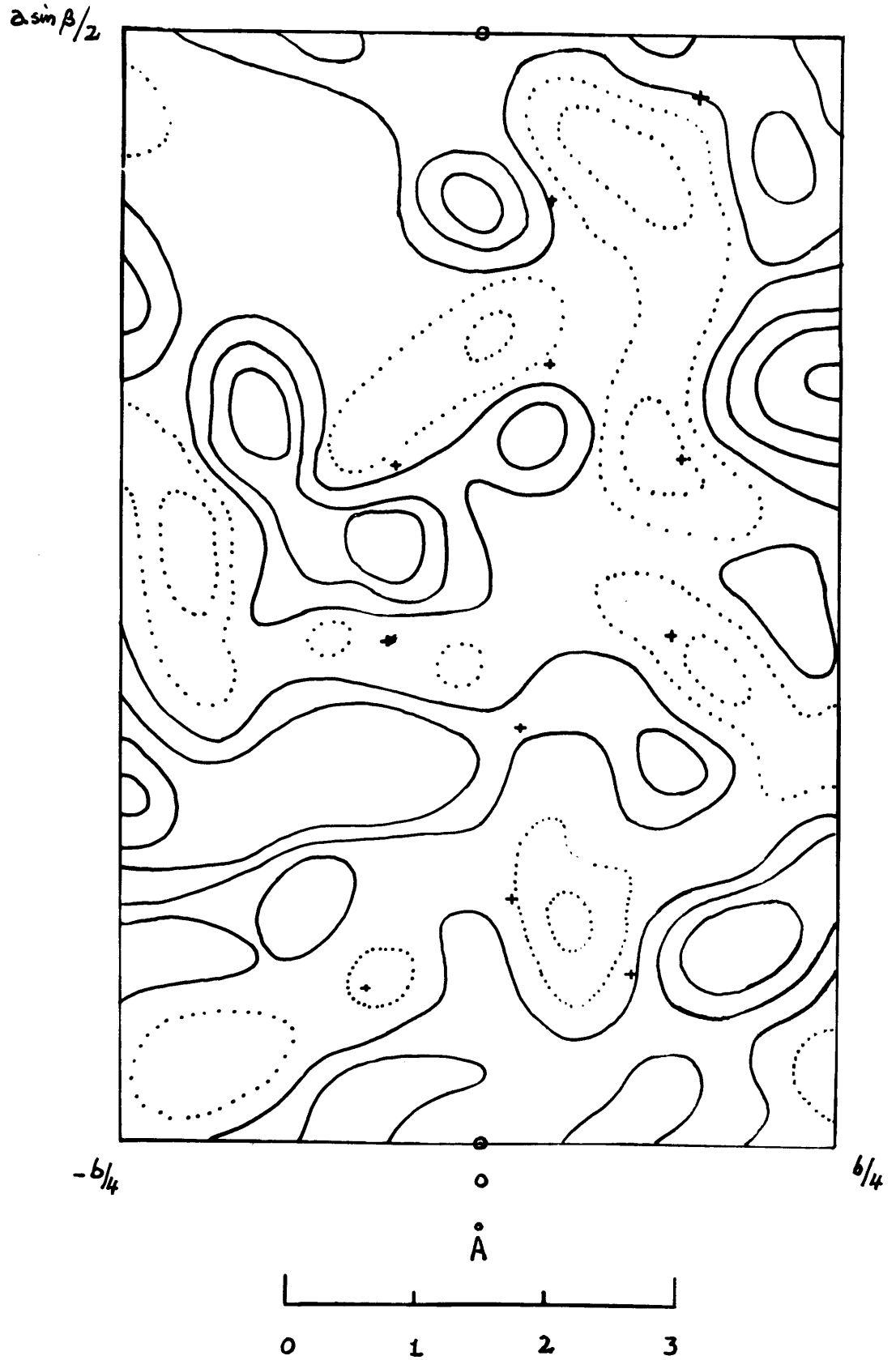
Table of fractional coordinates (hk0), anisic acid.

Atom	x/a	y/b
O(1)	0.0700	-0.0787
O(2)	.0770	.1099
O(3)	.4256	.0462
C(1)	.1102	.0208
C(2)	.1888	.0287
C(3)	.2270	- .0654
C(4)	.3060	- .0600
C(5)	.3500	.0447
C(6)	.3106	.1413
C(7)	.2297	.1330
C(8)	.4728	.1520

Fig. I6. Projection of residual electron density for (hkO) for anisic acid. Contours represent increments in electron density of 0.2 electrons per A^2; regions of negative density are indicated by broken lines.

Fig. I6. Projection of residual electron density for (hkO) for anisic acid. Contours represent increments in electron density of 0.2 electrons per A^2; regions of negative density are indicated by broken lines.




a sin β/2
-b/4
0
b/4
Å
0
1
2
3

The b axis projection.

The coordinates derived from the c axis projection enable a comparison to be made between the projected bond lengths, and the bond lengths which might reasonably be expected in such a molecule as this. It can be deduced from such a comparison that the molecule is probably planar, and that the axis of the molecule is tilted longitudinally to the plane (00I) by some 10°. The plane containing the benzene ring also appears to be inclined laterally to (00I) by some 25°.

Since the values of the x coordinates of the atoms are well established from the c axis projection it is therefore a fairly simple matter to decide on a suitable trial structure. Two orientations of the molecule are possible in this projection; it may lie either in the first quadrant or in the fourth. A choice was made between the alternatives by calculating structure factors for planes (h0l) where the value of (h0l) differed considerably from that of ($\bar{h}$0l) The fourth quadrant orientation was chosen as a result.

It is interesting to note in passing that this orientation was rapidly and easily checked in a qualitative manner by comparison of a weighted reciprocal lattice for the zone, and the Fourier transform for para-ethoxybenzoic acid which was at this point available.

A complete calculation of structure factors for the zone making use of the chosen trial structure was carried out and a good qualitative agreement was obtained between the observed and calculated data. The structure factor expression for the zone is given by :

$$F = 4f.\Sigma\cos 2\pi(hx + lz)$$

It was possible by this means to assign phase constants, $\pm I$, to 40 of the 52 observed terms.

These 40 terms were used as coefficients in a double Fourier synthesis, computed using Beevers Lipson strips at intervals of 6° (0.281 A.), along a , and of 12° (0.133A.) along c .

The electron density expression for (h0l) is given by:

$$\rho(h0l) = \frac{1}{A}\left[F(000) + 2\sum_{2}^{\infty}{}_{h}\, F(h00)\cos 2\pi hx + 2\sum_{1}^{\infty}{}_{l}\, F(00l)\cos 2\pi lz + \right.$$

$$\left. 2\sum_{2}^{\infty}{}_{h}\sum_{1}^{\infty}{}_{l}\left\{ F(h0l)\cos 2\pi(hx+lz) + F(\bar{h}0l)\cos 2\pi(-hx+lz)\right\}\right].$$

The resulting electron density distribution was plotted but was not very informative, severe overlap occuring between two molecules in projection. A second such synthesis based on structure factors calculated from the first did not noticeably improve in appearance, and it was decided to proceed immediately to ($F_o - F_c$) syntheses to attempt to improve matters. The value of R in the usual terms, was at this stage 25% . Two such syntheses were carried out and the results embodied in structure factor calculation. The value of R was 22% .

At this point the refinement was concluded since attention was drawn to a paper by Mr. J.P.G. Richards of the University College of South Wales, (v), describing

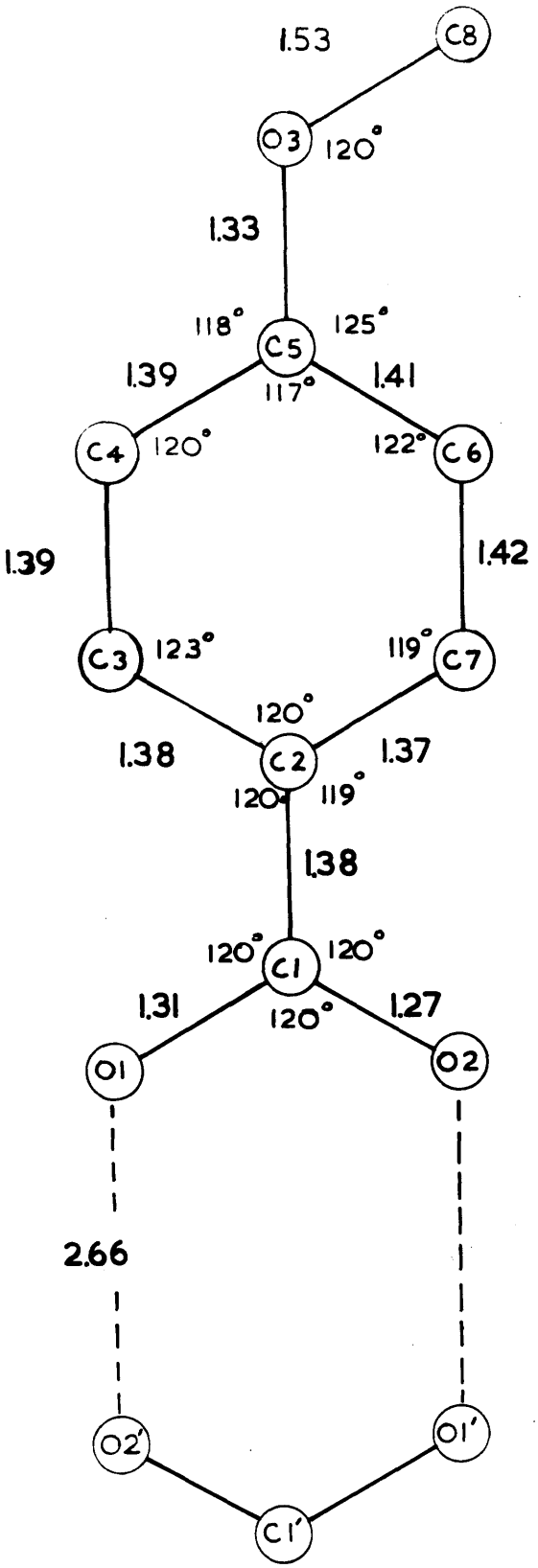


Fig. I7. Diagram illustrating the bond lengths (Angstrom units), and inter-bond angles found for anisic acid.

a preliminary analysis of the structure of anisic acid by X - ray methods. Correspondance with Richards revealed that he was refining the structure by least squares methods and that this process was fairly well advanced.

Bond lengths and bond angles etc. in anisic acid.

A brief word is neccesary as to the procedure adopted in calculating the bond lengths given in the following pages. It was initially assumed that the molecule of anisic acid is planar. An equation for the mean molecular plane was then calculated by least squares methods. This equation was given by :

$$x - 1.746y + 3.916z + 1.590 = 0$$

The deviations of individual atoms from this plane were then calculated and it became apparent that the molecule was probably not truly planar, deviations from the plane being calculated as large as 0.25 A., and that the deviations were consistent with a molecule planar except for the methyl group.

A fresh mean plane was calculated for all atoms except the methyl carbon atom, given by the equation :

$$x - 1.371y + 3.213z + 0.451 = 0$$

The average deviation from this plane, excluding the methyl carbon atom, was 0.023 A., and the greatest was 0.06 A. The methyl carbon atom deviates from this plane by 0.297A. New values of the z coordinate of all atoms except the methyl carbon atom were then calculated assuming the molecule to be truly planar. The situation with regard to the remaining atom is somewhat ambiguous; If it be assumed to

be coplanar with the remainder of the molecule the structure factor agreement deteriorates from a value of R = 22 % , to one of R = 29 % , but on the other hand if the molecule is assumed to be non-coplanar then the length of the C - O bond involving the atom in question, I.53 A., is longer than any recognised value, and compares unfavourably with the value of I.43 A. given by the planar model. For the present purposes a non planar structure has been assumed although the present state of refinement makes it unwise to assume the reality of one form as confirmed.

The bond lengths and inter-bond angles are given in the figure overleaf. Standard deviations in atomic position have not been calculated, but from the bond length variations within the benzene ring the accuracy of the measured values for the bond lengths is probably of the order of $\pm$ 0.03 A.

It is possible that the observed difference in the C - O bonds in the carboxyl group is not real but indicates a disorder identity of the type found in benzoic acid (vi). The bond C(I) - C(2) is shorter than a typical single bond value, approaching in fact a nearly total aromatic character. The bond C(5) - O(3) is also shortened for similar reasons and compares with the length of I.36 A. found in the molecule of di-methoxybenzene (vii). The situation as regards the bond O(3) - C(8) has already been discussed. No evidence was forthcoming for bond length variations in the benzene ring of the type claimed by the workers on di-methoxybenzene, and the values found are quite normal.

The inter-bond angles call for little comment, all are of the magnitude expected ; the equality of angles about the carboxyl group lends support to the idea of disorder

already suggested. The inter - molecular separations, and the arrangement of molecules are illustrated in the diagram overleaf. The molecules are linked in pairs in the normal fashion for carboxylic acids, the length of the hydrogen bond being 2.66 A., which is fairly typical.

Interest attaches to the approach between the atoms O(3) and O(3"). This is the shortest non-bonded approach and the value of 2.97 A. is only just greater than twice the van der Waal's radius of the oxygen atom, illustrating a very economical packing of molecules. Other approach distances are normal and call for no comment, save to remark that for those approaches which involve C(8) equally acceptable values result whatever value of the z coordinate for that atom, between the two extremes discussed, is used.

At the time of writing no further information is available as to the state of the work on this compound being done in Wales, and the possibility of an interesting comparison between two different methods of refinement is therefore excluded.

Table of fractional coordinates for (h0l) for anisic acid resulting from the second (F_o - F_c) synthesis.

Atom	x/a	z/c
O(1)	0.0745	-0.1742
O(2)	.0770	+ .0404
O(3)	.4256	- .3586
C(1)	.1102	- .1159
C(2)	.1888	- .1741
C(3)	.2270	- .3041
C(4)	.3094	- .3815
C(5)	.3500	- .2980
C(6)	.3135	- .1463
C(7)	.2331	- .0781
C(8)	.4738	- .1919

The conversion of these coordinates to orthogonal coordinates was accomplished firstly by conversion to Ångstrom units, and then by application of the formulae :

$$X = x.\sin\beta$$
$$Z = z - x.\cos\beta$$

The table overleaf gives the final values of X, Y, and Z used in the calculation of bond lengths and angles. In deriving X, the values of x/a obtained from the (hk0) projection were used in preference to an average of those from each zone owing to the much higher accuracy obtaining in (hk0).

Table of values of X, Y, and Z, in Ångstrom units, and referred to orthogonal axes, used in the calculation of bond lengths, inter-bond angles, and inter-molecular approach distances etc., in anisic acid.

Atom	X	Y	Z
O(I)	I,I8I	-0.865	-0.877
O(2)	I.299	I.208	-0.029
O(3)	7.I8I	0.508	-2.I59
C(I)	I.859	0.229	-0.62I
C(2)	3.I86	0.3I5	-0.997
C(3)	3.830	-0.7I9	-I.639
C(4)	5.I63	-0.659	-2.028
C(5)	5.905	0.49I	-I.769
C(6)	5.240	I.553	-I.I09
C(7)	3.875	I.462	-0.723
C(8)	7.977	I.670	-I.588

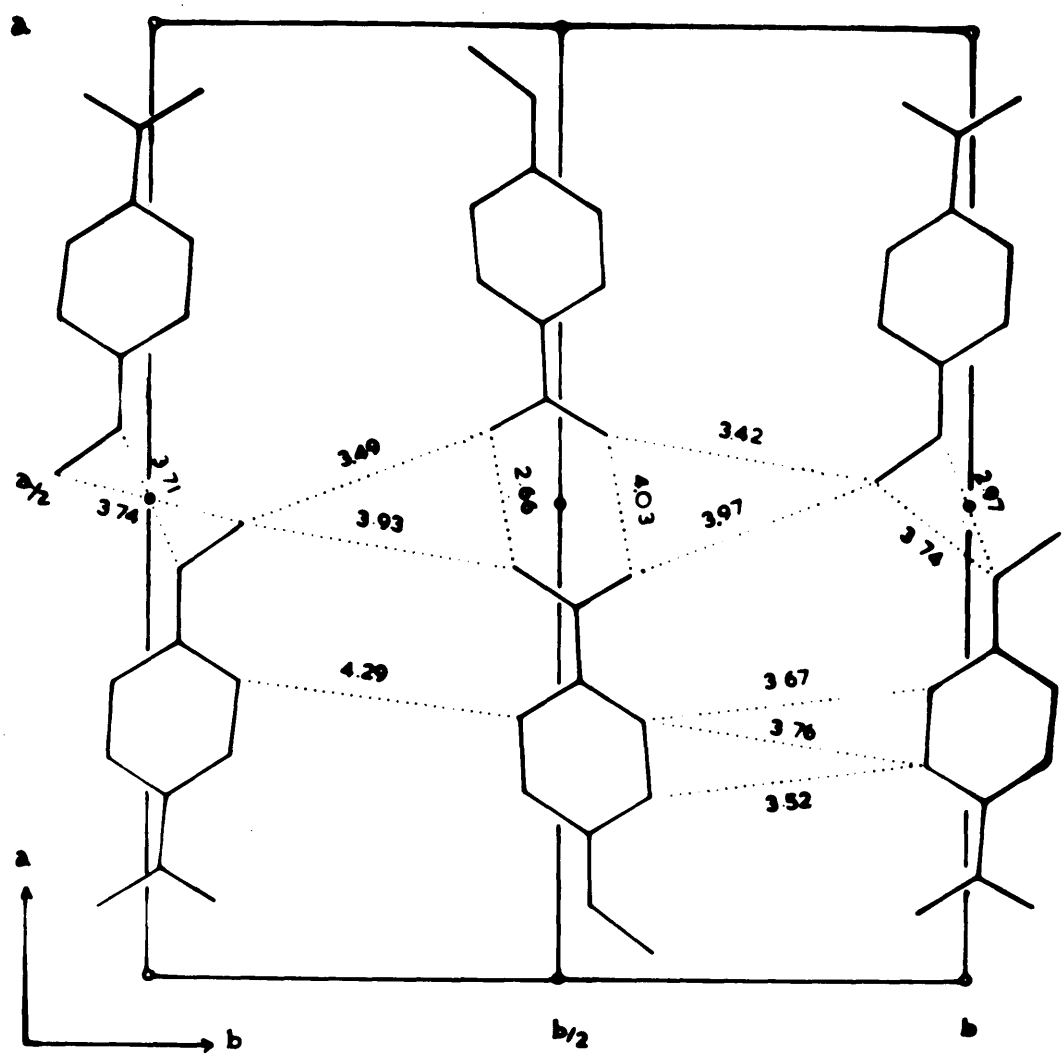


Fig. I8. Diagram illustrating the arrangement of molecules of anisic acid in (hk0) projection and giving the distances of closest approach between molecules. Figures in the left sector refer to molecules related by z and ± z; those in the right sector to molecules related by z and z ± I .

Table of inter-molecular approach distances between molecules of anisic acid.

Between molecules (x,y,z) and $(\bar{x},\bar{y},\bar{z})$.

O(I)...O(2')	2.66 A.	(hydrogen bond)	

Between molecules $(x,y,z,)$ and $(I - x,\bar{y},\bar{z},)$

O(3)...O(3')	3.7I A.		
C(8)...C(8')	3.74 A.		

Between molecules $(X,y,z,)$ and $(½ - x, ½ + y,\bar{z},)$

C(8)...O(I')	3.93 A.		
C(6)...C(3')	4.29 A.		

Between molecules $(x,y,z,)$ and $(½ + x,½ - y,z,)$

C(8)...O(2')	3.49 A.		

Between molecules $(x,y,z,)$ and $(\bar{x},\bar{y},\bar{z} - I)$

O(I)...O(2')	4.03 A.		

Between molecules $(x,y,z,)$ and $(½ - x, ½ + y, \bar{z} - I)$

C(6)...C(3')	3.52 A.	C(8)...O(I')	3.42 A.
C(7)...C(3')	3.76 A.		
C(7)...C(4')	3.67 A.		

Between molecules $(x,y,z,)$ and $(½ + x, ½ - y, \bar{z} - I)$

C(8)...O(2')	3.97 A.		

Between molecules $(x,y,z,)$ and $(I - x,\bar{y},\bar{z} + I)$

O(3)...O(3')	2.97 A.		
C(8)...O(3')	3.74 A.		

References : Part Two, Section Two.

I. P. Groth : Chemische Kristallographie, IV, 504.

ii. T.C. Downie, T. Palmer : unpublished work, Glasgow, I953.

iii. J.M. Robertson : J. Sci. Instr. (I943), 20, I75.

iv. A.J.C. Wilson : Nature, (I942), I50, I52.

v. J.P.G. Richards : Research Correspondence, (I956) 9 .

vi. G.A. Sim, J.M. Robertson, T.H. Goodwin,: Acta Cryst., (I955), 8, I57.

vii. T.H. Goodwin, M. Przybylska, J.M. Robertson : ibid, (I950), 3, 279.

viii. I.L. Karle, H. Hauptman, J. Karle, A.B. Wing : ibid, (I957), I0; 48I.

7						
8						
9						
II	I.0I	3.8	- 4.8	8	[illegible]	[illegible]
I3	.I9	6.4	+ 7.I	9	I.00	4.4
I7	.55	8.9	+ I0.8	II	.08	9.9
		h20		I2	.I7	I4.3
0	0.28	60.6	+II0.2	I3	.25	83.4

Table of observed and calculated structure factors for (hk0) for anisic acid.

Index h	ζ	F_o	F_c	Index h	ζ	F_o	F_c
		h00					
2	0.I8	I4.8	- I8.2	4	0.46	29.I	- 28.6
4	.37	5.2	- 2.6	5	.53	I2.8	- 9.5
6	.55	3I.9	- 35.9	6	.59	26.2	- 25.0
8	.73	53.9	- 52.8	7	.69	6.0	- 7.2
I0	.9I	9.3	+ I0.I	8	.78	24.0	- 22.I
I2	I.I0	I4.7	+ I2.I	I0	.95	7.6	+ 6.9
I4	I.28	8.0	+ 7.8	II	I.04	3.9	+ 3.2
		hI0		I2	.I2	5.0	+ 5.4
I	0.I7	I0.I	+ 9.6	I3	.22	7.5	- 8.5
2	.23	I7.3	+ I8.2	I4	.30	5.5	+ 6.I
3	.3I	I.8	- 2.7			h30	
4	.39	9.0	+ I0.3	I	0.43	II.8	+ I5.7
5	.47	24.2	- 25.I	2	.46	I2.6	+ I8.2
6	.56	I3.7	+ I4.I	4	.55	23.5	+ 22.2
7	.65	36.0	- 38.4	5	.62	26.0	+ 23.5
8	.74	I7.7	+ I6.2	6	.76	2.9	+ 4.9
9	.84	I9.8	+ 20.4	7	.92	I6.I	+ I3.9
II	I.0I	3.8	- 4.8	8	I.00	-	-
I3	.I9	6.4	+ 7.I	9	I.00	4.4	+ 6.2
I7	.55	8.9	+ I0.8	II	.08	5.5	+ 7.5
		h20		I2	.I7	I4.3	- I7.4
* 0	0.28	60.6	+II0.2	I3	.26	23.4	- 22.6
I	.30	35.4	- 40.3	I4	.34	4.8	+ 5.7
2	.34	I0.6	- I0.6				
3	.39	23.7	- 24.4				

Index	ζ	F_o	F_c
	h40		
h			
0	0.56	31.3	+ 32.2
I	.57	I3.9	+ I0.6
2	.59	6.6	- 6.0
3	.62	29.8	- 3I.3
4	.66	28.9	- 28.I
5	.72	28.0	+ 25.4
6	.78	9.3	+ II.4
7	.88	8.3	+ I0.4
8	.92	7.5	+ 8.4
9	.99	3.3	+ I.2
I0	I.07	3.5	+ 4.4
II	.I4	9.3	+ I0.4
I2	.22	4.2	- 4.0
I3	.30	3.9	+ 2.7
I4	.39	4.0	- 4.3
	h50		
I	0.70	I9.8	- I8.7
2	.72	I5.3	+ I2.2
3	.75	I7.0	- I6.6
4	.79	27.4	+ 30.7
5	.83	I2.8	+ I5.6
6	.89	6.0	- 7.3
7	.94	2I.7	+ 22.5
8	I.0I	I0.5	- I3.3
9	.08	8.4	+ 6.3
I0	.I5	5.2	- 3.8
II	.22	33.9	- 35.3

Index	ζ	F_o	F_c
		h 5 0	
I2	I.30	I7.3	- I8.8
I3	I.37	I6.0	+ I5.8
		h 6 0	
0	0.84	II.3	- I0.2
I	.85	3.6	+ 7.7
2	.86	5.9	- 2.9
3	.88	20.7	- I9.9
5	.95	I9.9	+ 20.6
6	I.00	20.2	+ I8.8
8	.II	9.4	+ 8.2
I0	.24	5.4	+ 6.0
II	.37	4.3	+ 4.6
I2	53	I5.4	- I3.3
		h 7 0	
I	0.98	3.9	- 4.2
2	I.00	6.9	+ 7.8
3	I.0I	9.0	- I3.I
4	.04	I6.3	+ I7.6
5	.07	7.2	- 5.3
I2	I.47	I6.4	- I7.5
		h 8 0	
0	I.I2	7.4	- 6.7
I	I.I3	20.0	- 20.7
2	I.I4	4.I	+ I.I
3	.I6	6.2	- 6.8
		h 9 0	
I	I.27	I7.2	+ I5.7
2	I.28	4.3	- 4.2
8	I.46	7.7	+ I0.0

Index	ζ	F_o	F_c	Index	ζ	F_o	F_c
		h,IO,O					
0	.4I	I8.0	- I7.5				
I	.4I	20.0	- I8.8				
2	.42	9.0	+ 6.8				
3	.44	4.5	+ 4.0				
4	.45	4.5	- 4.6				
5	.47	5.7	- 5.5				
6	.50	7.3	- 6.0				
		h,II,O					
I	I.55	9.4	+ 8.9				
2	.55	IO.4	- II.0				
		h,I2,O					
0	I.69	7.2	- 6.0				
I	.69	4.2	- 3.7				

Table of observed structure amplitudes and calculated structure factors for (hOl) for anisic acid.

Index h	ζ	F_o	Fc	Index h	ζ	F_o	Fc
		h,0,0				$\bar{h}$,0,I	
2	0.I9	I5.5	- I4.7	6	0.63	I6.7	- 23.7
4	.38	5.7	- I.I	8	.79	I8.0	+ I2.2
6	.56	35.9	- 32.0	I0	.96	6.4	- 6.2
8	.74	60.5	- 54.4	I2	I.I3	II.6	+ I0.7
I0	.93	I0.7	+ 8.6	I4	.32	5.6	+ 3.4
I2	I.09	I7.3	+ I5.5	I6	.48	I7.5	+ I4.4
I4	.3I	II.8	- I3.9	I8	.66	4.8	- 2.8
I6	.48	3.3	+ 5.6	20	.84	5.5	- 9.9
I8	.67	9.5	- 6.7			h,0,2	
20	.85	5.7	- 8.3	0	0.78	I9.2	- 22.5
		h,0,ℓ		2	.82	22.7	+ 33.4
0	0.38	52.4	+ 52.9	4	.9I	I0.5	+ 3.9
2	.45	5.3	- 3.9	6	I.02	I2.I	- 9.6
4	.57	6.8	- 2.6	8	.I3	4.2	- 4.3
6	.72	I6.9	- I6.2	I0	.28	3.2	- 4.2
8	.88	2I.7	- 25.I			$\bar{h}$,0,2	
I0	I.05	I3.0	+ I2.5	2	0.78	24.6	- 30.0
I4	.40	5.9	- 4.4	4	.82	I7.4	- I2.5
I6	.57	7.5	- 7.9	6	.90	I8.0	+ I4.3
I8	.75	3.7	+ 2.2	8	I.02	I3.7	+ I5.6
		$\bar{h}$,0,ℓ		I0	.I3	3.2	+ 8.9
2	0.42	23.5	+ 22.0				
4	.5I	5.6	+ 2.4				

Index h	$\sin\theta/\lambda$	F_o	F_c
	h,0,3		
0	I.I7	5.5	- 0.3
4	.28	4.5	- 4.I
6	.36	I7.5	- I3.9
8	.46	6.5	+ 6.I
I0	.57	5.5	+ 6.2
	$\bar{h}$,0,3		
4	I.I9	3.0	- 0.8
I0	.40	I5.I	- I6.3
I2	.52	5.5	+ 6.4
	h,0,4		
0	I.55	8.4	- I0.4
6	.72	3.8	+ 2.3
	$\bar{h}$,0,4		
2	I.55	I3.2	+ I2.3
8	.72	6.6	+ 8.5
I0	.80	I5.3	+ I6.3

PART TWO

SECTION THREE

The Crystal and Molecular Structure of para-ethoxybenzoic acid in part.

para-ethoxybenzoic acid.

Introductory and Crystal Data.

The second acid in the series to be studied was para-ethoxybenzoic acid. No record exists of any previous structural work on this compound.

The unit cell dimensions have been determined from rotation and oscillation photographs taken about the three principle axes using Copper K radiation, (λ = I.542A.), and the space group symmetry has been deduced from systematic absences on moving films of the Weissenberg type. The relevant crystal data are tabulated below.

Table of Crystal Data for para-ethoxybenzoic acid.

$C_2H_5O.C_6H_4.COOH$. Mol.wt. = I66.I7, F(000) = 342,

m.p. = I95°.

Monoclinic prismatic :

a = 22.04, b = 4.0I, c = 9.47 A.

β = 98° V = 828.8 A^3.

$\rho_{obs.}$ = I.323 ; ρ calculated for four molecules per unit cell = I.324

Systematic absences : (h0l) when h = 2n + I.

(0k0) when k = 2n + I.

Space group : $P2_1/a$.(C_{2h}^5.)

Intensity Data.

Intensity data for (h0l) were collected using the Robertson Multiple Film Technique, as described in the previous section. The reduction factor used was 3.I5.

122 out of a theoretically accessible 229 reflexions were recorded in (hol), giving a ratio of reflexions to positional parameters, excluding hydrogen atoms, of ca. 5:1.

Structure amplitudes were derived in the usual way, and were placed on an absolute scale, initially by Wilson's method (i), and later by comparison with the calculated values. The value of the Debye-Waller temperature factor B derived by this method was 3.5. Since the crystal used had an approximately cylindrical cross section, no corrections for absorbtion were applied.

Structural Work.

From the superficial resemblance in the cell dimensions of this acid and anisic acid, it might be thought that the structure of this acid could be derived from that of anisic acid simply by making allowance for the presence of an extra carbon atom, in an otherwise iso-structural arrangement.

That this is not the case however, is rapidly shown by comparison of the Fourier transform for the acid with the weighted reciprocal lattice (h*o l*).

For purposes of calculation of the transform, an idealised structure was adopted for the acid, embodying a planar dimer with all bond lengths taken as 1.36 A. and the oxygen - oxygen hydrogen bonded distance assumed 2.72 A. All inter-bond angles were taken as 120°.

Since the dimer is centro-symmetric, the transform will everywhere be real. The centre of symmetry was taken as origin and axes X and Y were chosen , in the plane of the molecule, as illustrated in Figure 19, overleaf.

If the co-ordinates of the jth atom be (x_j, y_j) with respect to the axes X and Y, then the transform is given by:

$$T(X,Y) = 2\sum_{j=1}^{N/2} N_j . \cos 2\,(x_j X + y_j Y)$$

The x co-ordinates of all atoms are multiples of 0.68 A., and the y co-ordinates are multiples of I.I8 A. . If these lengths are used as the units of distance on the X and Y axes respectively, the transform is periodic in the XY plane with repeat distances of I.47 A^{-I}, along X, and 0.85 A^{-I} along Y.

The function actually evaluated, by means of Beevers-Lipson strips, was :

$$\begin{aligned} T(X,Y) = {} & 8\left[\cos(2X + Y) + \cos(2X - Y) + \cos \right] \\ & + 6\left[\cos 3X + \cos 5X + \cos 9X + \cos(6X + Y) \right. \\ & + \cos(6X - Y) + \cos(8X + Y) + \cos(8X - Y) \\ & \left. + \cos(12X + Y) + \cos(14X + Y) \right] \end{aligned}$$

The interval of evaluation was 6° along each axis.
In the b axis projection, the relation between structure amplitude and transform is given by :

$$F(h0l) = 2.f.T(X,Y)$$

where f is a scattering function and T(X,Y) is the value of the transform at the position corresponding to the reciprocal lattice point (h0l) .

The (h0l) weighted reciprocal lattice, i.e. with values = F (h0l)/2.f, was readily oriented on the transform, in the manner illustrated in Fig, I9, and the signs of I02 of

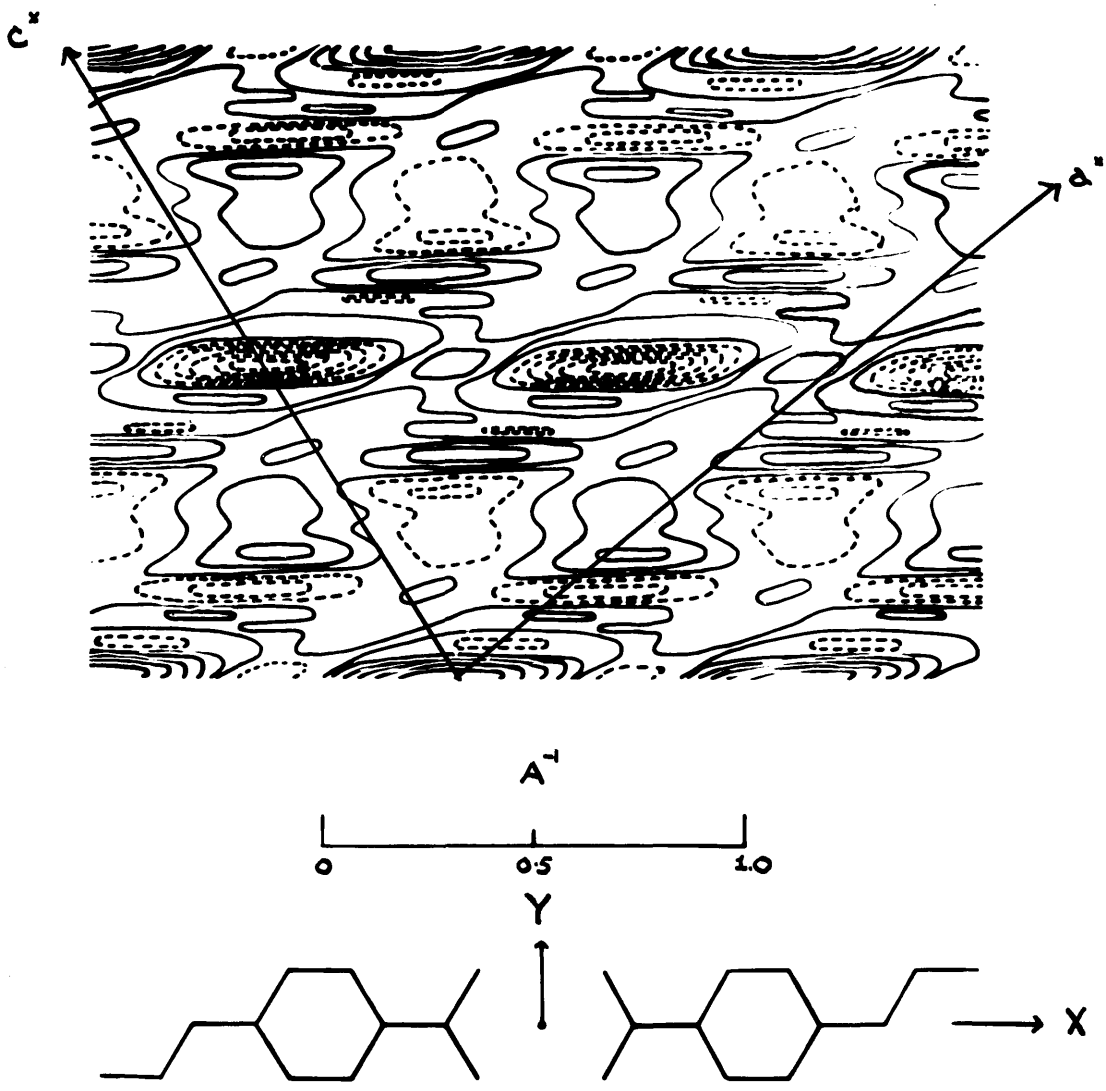


Fig. I9. Fourier transform of idealised molecule of para-ethoxybenzoic acid , showing choice of molecular axes and orientation of reciprocal axes. Negative contours are broken.

the I22 structure factors were held to be fixed. These structure factors were then used as coefficients in a two dimensional Fourier synthesis, evaluated using Beevers-Lipson strips at 6° intervals along each axis, using the expression for the electron density in (hOl) for the space group $P2_1/a$ given in the previous section.

Immediate resolution of all atoms was achieved in the resulting contour map of electron density, and a complete calculation of structure factors was carried out using atomic centres derived from this map.

All I22 terms were included in a second synthesis evaluated in a similar manner at intervals of 3° along a and 6° along c . This resulted in an improved projection of electron density and the process of structure factor calculation was repeated, and a third Fourier synthesis carried out in the same way as previously.

The projection of electron density resulting from this third synthesis is shown in Fig. 20.

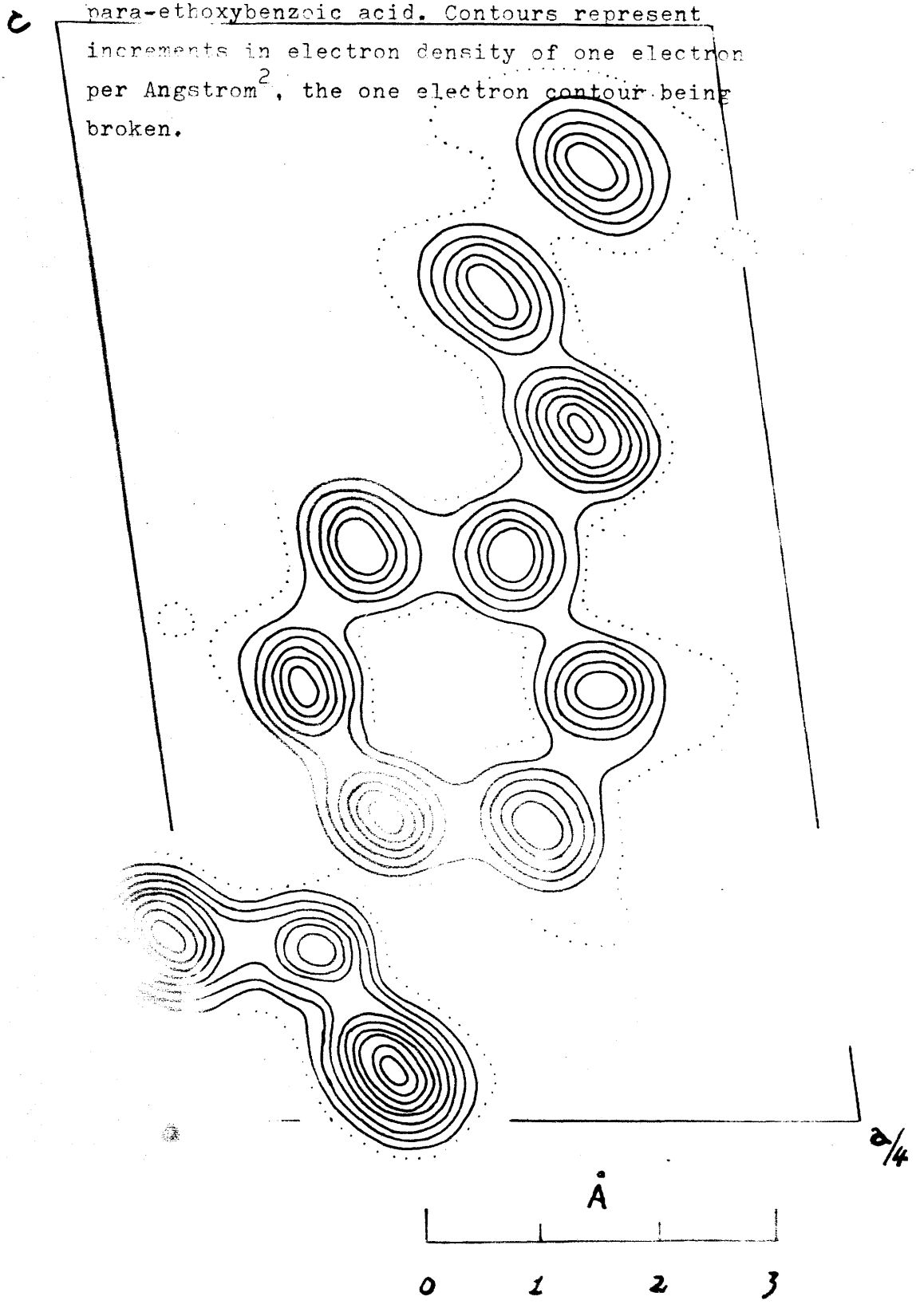
Structure factor calculation based on the current atomic centres chosen from this projection give a value for R in the usual terms of I8 %.

The value of R fell in the three calculations of structure factors in the sequence : 28 % → 22 % - I8 %.

At this point the refinement rests.

Fig. 20. Projection of electron density for (hCl) for para-ethoxybenzoic acid. Contours represent increments in electron density of one electron per Angstrom^2, the one electron contour being broken.

Fig. 20. Projection of electron density for (hCl) for para-ethoxybenzoic acid. Contours represent increments in electron density of one electron per Angstrom^2, the one electron contour being broken.



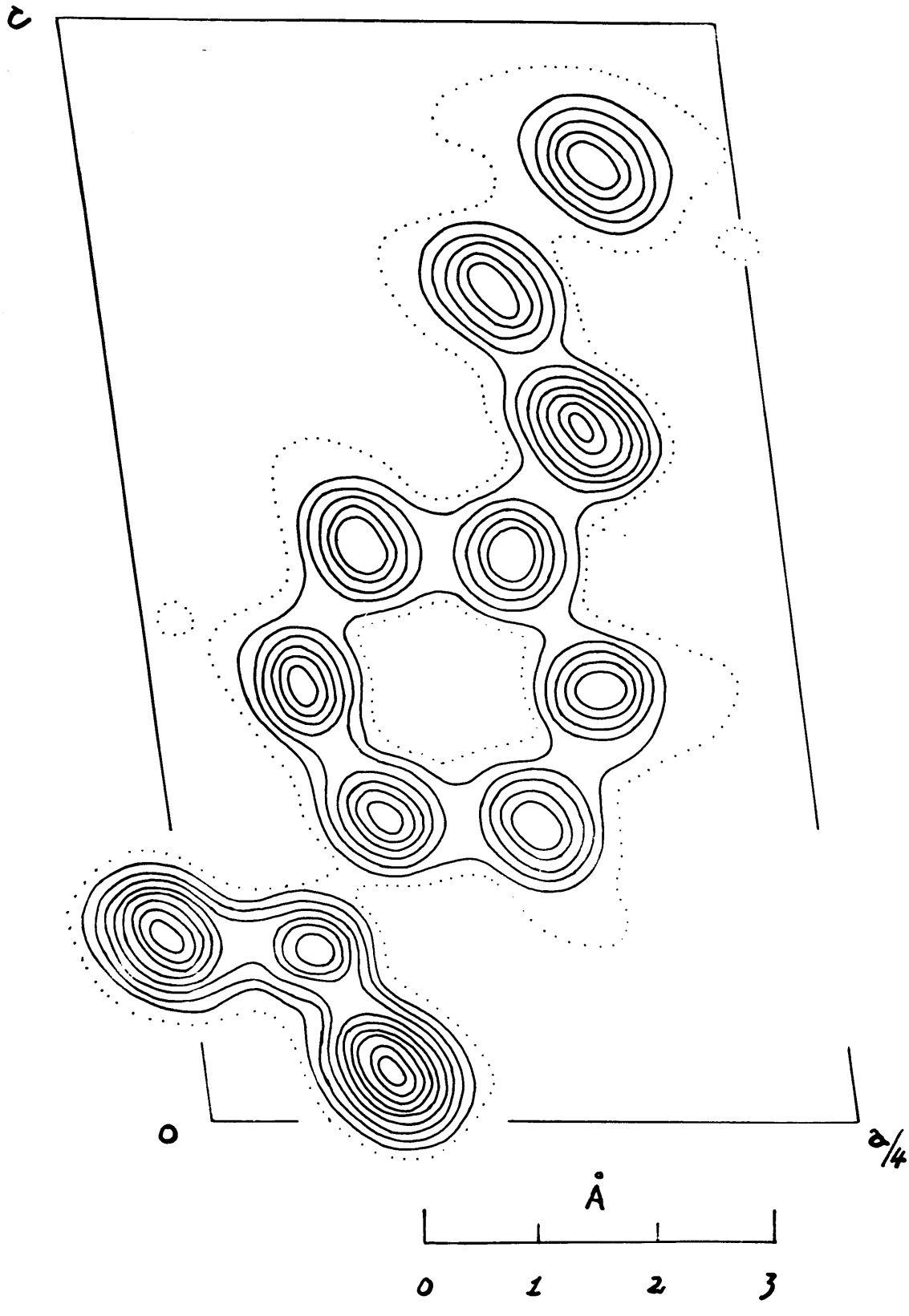

c
0
a/4
Å
0
1
2
3

Table of fractional coordinates for (h0l) for para-ethoxybenzoic acid.

Atom	x/a	z/c
O(I)	0.07I7	0.0486
O(2)	- .0064	.I694
O(3)	.I782	.6332
C(I)	.0505	.I546
C(2)	.0823	.2754
C(3)	.0570	.40I8
C(4)	.0895	.52I0
C(5)	.I468	.5I46
C(6)	.I736	.3924
C(7)	.I407	.27I2
C(8)	.I53I	.7562
C(9)	.I982	.8674

****